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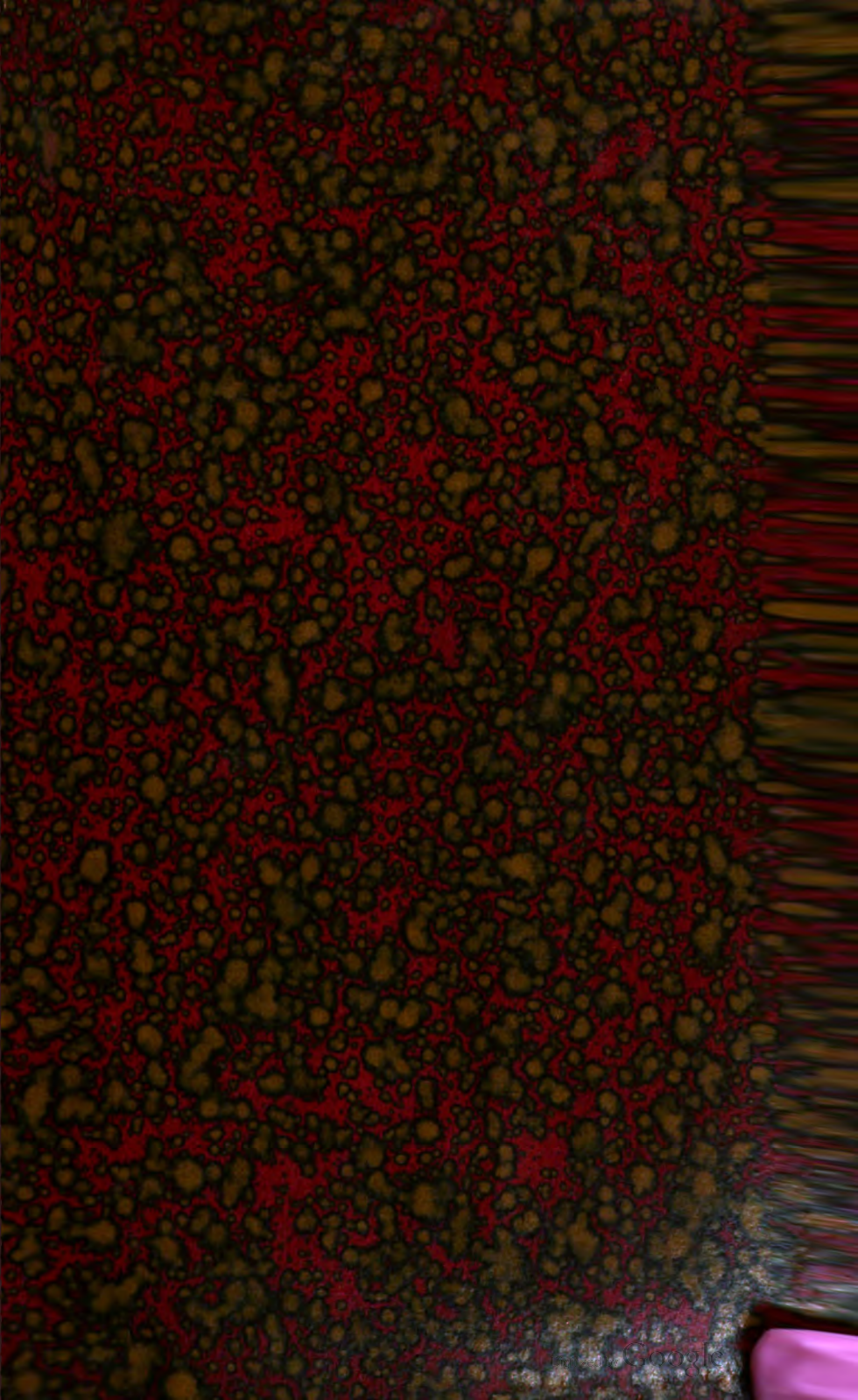
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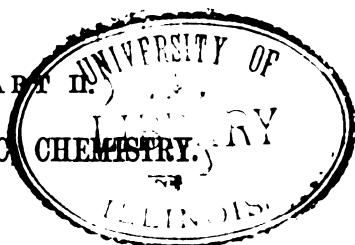
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(PART II.)

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*The reader is requested to make the following corrections  
in Part II.*

Page	8,	8 lines from top,	for nitron read nitron.
"	68, 3	" "	bottom, for $3\text{H}_2\text{O}$ read $2\text{H}_2\text{O}$ .
"	86, 5	" "	top, for $\text{CO}, \text{CuCl}, \text{H}_2\text{O}$ read $\text{CO}, \text{Cu}_2\text{Cl}_2, 2\text{H}_2\text{O}$ .
"	96,	last line of table,	for $3\text{HgNO}_2, \text{HgHO}$ read $3\text{HgNO}_2, \text{Hg}_2\text{O}, \text{H}_2\text{O}$ .
"	122,	12 lines from top,	for 350, read 700, and for 6 read 12.
"	128, 6	" "	for 18'60 read 81'60.
"	135, 16	" "	for sodium read potassium.
"	"	17 and 18	each time, for Na read K.
"	"	17 lines from top,	dele $\text{H}_2\text{O}$ sometimes with $5\text{H}_2\text{O}$ .
"	185,	in table,	for 25 read 35.
"	255,	19 lines from bottom,	for $5\text{H}_2\text{O}$ read $10\text{H}_2\text{O}$ .
"	289, 17	" "	for 1'45 read 1'247.
"	311,	in table,	fusing point of antimony, transpose 1150 and 621.
"	332,	13 lines from top,	for three read two.
"	345,	in table,	for $\text{SbS}_3$ read $\text{Sb}_2\text{S}_3$ .
"	351,	11 lines from top,	for $\text{Cr}_2\text{Cl}_3$ read $\text{Cr}_2\text{Cl}_2$ .
"	366, 8	" "	bottom, for $\text{HNO}_3$ read $2\text{HNO}_3$ .
"	367,	last line second table,	for $\text{Al}_2$ read $\text{Al}$ .
"	399,	6 lines from bottom,	for $\text{K}_2\text{CO}_3$ read $\text{K}_2\text{CO}_2$ .
"	430, 8	" "	for $2(\text{Al}_2\text{O}_3 + 5\text{SiO}_2)$ read $2\text{Al}_2\text{O}_3 + 45\text{SiO}_2$ .
"	465, 5	" "	top, for $108'5 + 198$ read $158'5 + 108$ .
"	514, 8	" "	bottom, for $51'27$ read $51'17$ .
"	533,	table in heading,	for $^{\circ}\text{C}$ . read $^{\circ}\text{C}$ .
"	540,	10 lines from bottom,	for $\text{CoCl}_2, 3[(\text{H}_4\text{N})_2\text{O}]$ read $\text{CoCl}_2, 6\text{H}_2\text{N}, \text{H}_2\text{O}$ .
"	541, 20	" "	for $7\text{H}_2\text{O}$ read $5\text{H}_2\text{O}$ .
"	607,	3 lines from top,	for $\text{NaHCrO}_4, \text{H}_2\text{O}$ read $2(\text{NaHCrO}_4), \text{H}_2\text{O}$ .
"	610,	last line,	for $2\text{K}_2\text{C}_2\text{O}_4$ read $2\text{K}_2\text{C}_2\text{O}_4$ .
"	643,	6 lines from top,	for 186'8 read 231'5.
"	701, 21	" "	for $\text{Cu}_2\text{P}_2$ read $\text{Cu}_2\text{P}_4$ .
"	703, 13	" "	for $(\text{H}_4\text{N})$ read $(\text{H}_4\text{N})_2$ .
"	713, 7	" "	from bottom, for conduct read condense.
"	743, 16	" "	from top
"	745, 6	" "	from bottom } sal alembroth, for $6\text{H}_4\text{NCl}$ read $2\text{H}_4\text{NCl}$ .
"	799, 5	" "	from top, for $2\text{H}_2\text{O}$ read $\text{H}_2\text{O}$ .
"	"	11	" add $\text{H}_2\text{O}$ at end of line.
"	819, 6	" "	from bottom, for $20^{\circ}$ read $30^{\circ}$ .
"	831, 7	" "	from bottom, for 1865, 1866, read 1866, 1867.
"	861, 2	" "	from top, for 0'515 read 1'304.
"	868, 22	" "	from top, for cases read causes.

*Additional Corrections in Part I.*

Page	154,	13 lines from top,	for 16 read 13.
"	204,	in note for $\frac{(420+t)V'}{500}$	read $\frac{510V'}{420+t}$
"	401,	13 lines from top,	after bars add possessing equal moments of inertia about their points of suspension.
"	"	18	" for magnets read magnetic poles.
"	"	19	" for their read the.



*Symbols and Atomic Weights of the Elements  
as used in this Volume.*

Names of Elements.	Symbol.	At. wt.	Names of Elements.	Symbol.	At. wt.
Aluminum . .	Al	27.5	Molybdenum .	Mo	96
Antimony . .	Sb	122	Nickel . . .	Ni	59
Arsenicum . .	As	75	Niobium . .	Nb	94
Barium . . .	Ba	137	Nitrogen . .	N	14
Bismuth . . .	Bi	210	Osmium . . .	Os	199
Boron . . . .	B	10.9	Oxygen . . .	O	16
Bromine . . .	Br	80	Palladium . .	Pd	106.5
Cadmium . . .	Cd	112	Phosphorus .	P	31
Cæsium . . . .	Cs	133	Platinum . .	Pt	197.1
Calcium . . .	Ca	40	Potassium . .	K	39.1
Carbon . . . .	C	12	Rhodium . .	Ro	104.3
Cerium . . . .	Ce	92	Rubidium . .	Rb	85.3
Chlorine . . .	Cl	35.5	Ruthenium . .	Ru	104.2
Chromium . . .	Cr	52.5	Selenium . .	Se	79.5
Cobalt . . . .	Co	59.0	Silicon . . .	Si	28
Copper . . . .	Cu	63.5	Silver . . . .	Ag	108
Didymium . . .	Di	96	Sodium . . .	Na	23
Erbium . . . .	E	112.6	Strontium . .	Sr	87.5
Fluorine . . .	F	19.0	Sulphur . . .	S	32
Glucinum . . .	G	9.5	Tantalum . .	Ta	182.0
Gold . . . . .	Au	196.6	Tellurium . .	Te	129
Hydrogen . . .	H	1	Thallium . .	Tl	204
Indium . . . .	In	75.6	Thorium . . .	Th	238
Iodine . . . .	I	127	Tin . . . . .	Sn	118
Iridium . . . .	Ir	197.1	Titanium . .	Ti	50
Iron . . . . .	Fe	56	Tungsten . .	W	184
Lanthanum . .	La	92	Uranium . . .	U	120
Lead . . . . .	Pb	207	Vanadium . .	V	51.3
Lithium . . . .	L	7	Yttrium . . .	Y	61.7
Magnesium . .	Mg	24.3	Zinc . . . . .	Zn	65
Manganese . .	Mn	55	Zirconium . .	Zr	89.5
Mercury . . .	Hg	200			



# PART II

## INORGANIC CHEMISTRY.

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### CHAPTER I.

#### NOMENCLATURE—CLASSIFICATION OF THE ELEMENTS.

(331) *Principles of Chemical Nomenclature.*—Before proceeding to a description of the chemical properties of the different elementary substances, and of the compounds which are the result of their union with each other, it will be needful to explain the principles upon which the nomenclature in use amongst chemists has been founded. The object of the inventors of this language was, not merely to give a distinguishing name to the substances spoken of, but also to convey a knowledge of their components, and even of the proportions in which those components occur. In the less complicated substances with which the chemist has to deal, this object is very completely attained. In those of a more complex nature, the employment of symbols (13) becomes necessary, in order that the composition of the body may be fully indicated; and the *formula* of a substance, especially if the substance be derived from the animal or the vegetable kingdom, becomes an indispensable supplement to its name.

1. *Elements.*—In the case of the elementary bodies, the common name of each is usually that by which it is distinguished in chemical language, if the substance—as is the case with many of the metals, such as lead, iron, copper, or zinc—be one which is familiarly known: if it be a body which the researches of the chemist have brought to light, the name is generally indicative of some marked peculiarity by which the element is characterized. Phosphorus, for example, is so named (from  $\phi\omega\varsigma$ ,  $\phi\omicron\rho\omicron\varsigma$ , light bearing) because when exposed to the air it emits a feeble light which is visible in a darkened room; iodine derives its name from  $\iota\omicron\epsilon\iota\delta\eta\varsigma$  (violet), in reference to the violet colour of its vapour; hydrogen (water producer, from  $\upsilon\delta\omega\rho$ ,  $\gamma\epsilon\nu\nu\acute{\alpha}\omega$ ) is so called from the circumstance that it is a necessary component of water; and so on.

The attempt to introduce a strictly systematic nomenclature for the elementary substances has failed, owing to the strong hold which the popular names of those in familiar use have retained upon the language; but in the case of the metals more recently discovered a common termination in *um* has been assigned to them, as, for example, palladium, iridium, osmium, potassium, sodium, aluminum, &c. Among the non-metallic elements analogies are also pointed out by a similarity in the termination of the name: for instance, chlorine, iodine, bromine, and fluorine, have similar properties; and the existence of a certain analogy between boron and silicon is indicated by the common termination of both.

2. *Binary Compounds*.—When elements combine with each other to form a binary compound—that is to say, a compound in which two elements only are present, and in which also one atomic proportion\* only of each substance is concerned—the nature of both the components is specified by the name employed: for instance, a combination of oxygen with zinc is designated oxide of zinc or zincic oxide. The following table will illustrate the manner in which such modifications are applied; the symbols of the different compounds are given in the fifth column. It is to be observed that in employing symbols the symbol of the basylous or electro-positive element (261) is usually placed first:—

The compounds of	are termed	For example:—		Or in symbols
Oxygen	Oxides	Zincic oxide, or	Oxide of zinc	Zn O
Chlorine	Chlorides	Argentio chloride	Chloride of silver	Ag Cl
Bromine	Bromides	Sodic bromide	Bromide of sodium	Na Br
Iodine	Iodides	Potassic iodide	Iodide of potassium	K I
Fluorine	Fluorides	Potassic fluoride	Fluoride of potassium	K F
Nitrogen	Nitrides	Boric nitride	Nitride of boron	B N
Carbon	{ Carbides or Carburets }	Nitric carbide (cyanogen)	Carbide of nitrogen.	C N
Sulphur	{ Sulphides or Sulphurets }	Cupric sulphide	Sulphide of copper	Cu S
	{ Selenides or Seleniurets }	Plumbic sulphide	Sulphuret of lead	Pb S
Selenium	{ Phosphides or Phosphurets }	Mercuric selenide	Selenide of mercury	Hg Se
Phosphorus		Cadmio selenide	Seleniuret of cadmium	Cd Se
		Calcio phosphide	Phosphuret of calcium	Ca P

\* We have already called attention (12a) to the loose way in which the terms *atom* and *equivalent* are often employed by chemists, and have pointed out the essential difference between the signification of the two terms. For example, an acid like the citric ( $\text{H}_3\text{C}_6\text{H}_7\text{O}_7$ ), will require three times as much potassium to form with it a neutral salt, as is required by another acid, such as the nitric ( $\text{HNO}_3$ ). The proportion of citric acid represented by the formula ( $\text{H}_3\text{C}_6\text{H}_7\text{O}_7$ ) is nevertheless sometimes inaccurately termed its *equivalent*, and the same term is also applied to the proportion of nitric acid represented by the formula ( $\text{HNO}_3$ ); yet it is manifest that these quantities of the two acids are not equivalent to each other, inasmuch as one of them neutralizes three times as much potassium as the other.

In order, therefore, to avoid this solecism, and at the same time to secure

3. *Multiple Compounds*.—It often happens, however, in consequence of the operation of the law of multiple proportions (10), that the same pair of elements forms two or more compounds endowed with different properties, and which contain different proportions of their components: the electro-negative element in this case is usually the one in which the multiple relation is observed; and the number of atoms in which it enters into combination in the particular case is indicated by prefixing to the name an abbreviation of the corresponding Greek ordinal;  $\pi\rho\acute{o}\tau\omicron\varsigma$  first,  $\delta\epsilon\acute{\iota}\upsilon\tau\epsilon\rho\omicron\varsigma$  second,  $\tau\rho\acute{\iota}\tau\omicron\varsigma$  third, &c. For example, there are four different oxides of osmium:—

The first or lowest oxide is termed the osmium protoxide, or		} $\text{Os O}$
	protoxide of osmium	
The second oxide	„ osmium dioxide, or deut-	} $\text{Os O}_2$
	oxide of osmium . . .	
The third oxide	„ osmium trioxide, or tri-	} $\text{Os O}_3$
	toxide of osmium . . .	
The fourth oxide	„ osmium tetroxide, or tes-	} $\text{Os O}_4$
	saroxide, or peroxide of osmium . . . . .	

Sometimes the Latin prefixes are substituted for those derived from the Greek: thus the terms *binoxide* and *deutoxide* of tin are used indifferently for a combination ( $\text{SnO}_2$ ) of one atom of tin and two atoms of oxygen. In the same way *terchloride* of antimony ( $\text{SbCl}_3$ ) is used as synonymous with antimony *trichloride*. The more complicated relation of 3 atoms to 2 or  $1\frac{1}{2}$  to 1 is expressed by the Latin prefix *sesqui*, which means 'one and a half.' For example, we speak of *sesquisulphide* of iron ( $\text{Fe}_2\text{S}_3$ ), and chromium *sesquioxide* ( $\text{Cr}_2\text{O}_3$ ). The highest oxide, chloride, or sulphide, is frequently termed the *peroxide*, *perchloride*, or *persulphide*. For example, the compound  $\text{SbCl}_5$  is termed either antimony pentachloride or perchloride of antimony, and  $\text{CaS}_5$  is termed indifferently calcic persulphide or pentasulphide of calcium. This practice of using indifferently a Greek or a Latin prefix in the names of compounds belonging to the same series is etymologically reprehensible. If, for instance, the compound of tin ( $\text{SnS}$ ) be termed the *protosulphide*, the compound ( $\text{SnS}_2$ ) should, in order to preserve consistency, be termed the

brevity in our descriptions, it will be convenient to speak of the relative quantities of each acid above cited as an *atom* of their respective acids; a term warranted by the fact that the formula of each represents the simplest expression in symbols which can be adopted to indicate the smallest particle or atom of the compound which can exist either in combination or in a separate form.

*deutosulphide* or *disulphide*, though in this case the use of the name *bisulphide* is generally sanctioned by custom.

4. *Acids*.—If the oxides possess, when combined with the elements of water, acid characters, as, for example, is the case with some of the higher oxides of nitrogen, a different plan is adopted to mark this important peculiarity. At the time that the nomenclature was devised by Lavoisier and his coadjutors, oxygen was considered to be the element upon which the existence of the acid character mainly depended, as indeed its name (signifying generator of acids) implies. The system of nomenclature was therefore specially adapted to this idea. It frequently happens that an element forms more than one acid with oxygen: the compound which contains the largest proportion of oxygen is in this case indicated by making the name terminate in the syllable *ic*. Nitric acid ( $\text{HNO}_3$ ), for instance, is the acid of nitrogen in which the largest quantity of oxygen is found: in like manner sulphuric acid ( $\text{H}_2\text{SO}_4$ ) is the most highly oxidized acid of sulphur. A second acid which contains the same elements united with a smaller proportion of oxygen receives a name which ends with the syllable *ous*: thus nitrous acid ( $\text{HNO}_2$ ), and sulphurous acid ( $\text{H}_2\text{SO}_3$ ) indicate acids in which a smaller proportion of oxygen is present than in nitric and sulphuric acids. In a few cases an acid has been discovered which contains still more oxygen than the one to which the termination *ic* had been already appropriated. Chloric acid, for example, is represented as ( $\text{HClO}_3$ ), but an acid was subsequently found to exist, which has the composition ( $\text{HClO}_4$ ); in this case the prefix *per* (which is an abbreviation for  $\upsilon\pi\epsilon\rho$ , or *super*, above) is employed, and the new compound has been termed *perchloric acid*.\* When an acid is known in which the proportion of oxygen is smaller than that which exists in the compound to which the termination *ous* has been appropriated, the prefix *hypo* (from  $\upsilon\pi\omicron$  below) is usually employed—for instance, chlorous acid consists

---

\* The term acid has been employed by chemical writers up to a late period, to designate indifferently either the anhydrous bodies formed by the union of oxygen with the non-metallic elements, such as  $\text{CO}_2$  and  $\text{SO}_2$  (now commonly termed *anhydrides*, or bodies destitute of hydrogen), or the hydrated compounds produced by the action of water upon the anhydrides, such as  $\text{H}_2\text{SO}_4$ , oil of vitriol or sulphuric acid. To avoid this confusion, produced by the application of the same term to two substances essentially distinct, we shall limit the term acid to those hydrated bodies which are really salts of hydrogen: sulphuric acid,  $\text{H}_2\text{SO}_4$ , is then true dihydric sulphate, or sulphate of hydrogen; nitric acid,  $\text{HNO}_3$ , is hydric nitrate, or nitrate of hydrogen; acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , hydric acetate, or acetate of hydrogen, and so on.

of  $\text{HClO}_2$ , whilst the compound  $\text{HClO}$ , with a still smaller amount of oxygen is known as *hypochlorous acid*.

The progress of research, however, has revealed other acids in which oxygen is wanting, but which are compounds of hydrogen. These acids are usually distinguished by prefixing the word *hydro*, as an abbreviation for hydrogen: for instance, chlorine and hydrogen form an acid,  $\text{HCl}$ , *hydrochloric acid*, commercially often called *muriatic acid*: cyanogen and hydrogen form  $\text{HCy}$ , *hydrocyanic* or *prussic acid*, and so on. Some writers, following the example of Thénard, transpose these terms: they speak of *chlorhydic acid*, and *cyanhydic acid*.

5. *Salts*.—Owing to the change which has recently occurred in the views prevalent respecting the atomic constitution of chemical compounds, a good deal of confusion unfortunately exists at the present moment in the nomenclature adopted by different authors. This is nowhere more conspicuous than in the differences which prevail in the mode of designating the different varieties of salts.

At the time that our nomenclature was originally devised it was supposed that a salt consists of a combination of an acid with a basic oxide, and the name given to each salt was framed upon this idea; *sulphate of potash*, for example, indicated the salt formed by the action of sulphuric acid upon the alkaline base potash; *nitrate of soda*, the salt obtained by neutralizing nitric acid with soda. If the base has no single distinguishing name, as occurs with most of the insoluble oxides, a longer name was requisite. When, for instance, acetic acid acts upon oxide of copper, or formic acid upon oxide of lead, the salts procured were named, in accordance with the principle just explained, *acetate of oxide of copper*, and *formiate of oxide of lead*; but these long names became almost immediately shortened into *acetate of copper*, and *formiate of lead*; terms which are obviously inconsistent with the names given to the salts of the alkalies and of the earths.

Many chemists have sought to remedy this inconsistency by introducing in every instance the name of the basyl or the metal into the salt, instead of that of the base or metallic oxide. They speak therefore of *sulphate of potassium*, and *nitrate of sodium*, as well as of *acetate of copper* and *formiate of lead*.

Some writers, however, prefer, whilst still employing the name of the metal or basyl, to place it first in naming the salt, omitting the word of altogether; so that they speak of *potassium sulphate*, *sodium nitrate*, *copper acetate*, and *lead formiate*.

Lastly, Berzelius, for reasons to be explained immediately, not

only employs the name of the metal but modifies its termination ; so that he speaks of potassic sulphate, sodic nitrate, cupric acetate, and plumbic formiate.

It is this last modification which will generally be adopted in this work ; although cases will occasionally occur in which the other forms of nomenclature will be employed.

From what has been just stated, it will be seen that four different usages are more or less prevalent in naming salts ; these may be contrasted and compared together as in the following table :

$K_2SO_4$	{ Sulphate of potash, Dipotassic sulphate,	Sulphate of potassium, Potassium sulphate.
$NaNO_3$	{ Nitrate of soda, Sodic nitrate,	Nitrate of sodium, Sodium nitrate.
$Cu_2C_2H_3O_2$	{ Acetate of oxide of copper, Cupric diacetate,	Acetate of copper, Copper acetate.
$Pb_2CHO_2$	{ Formiate of oxide of lead, Plumbic diformiate,	Formiate of lead, Lead formiate.

When the acids by their action upon bases form salts, the degree of oxidation in the acid is still indicated by the name of the salt. When acids ending in *ic* form salts, in naming such compounds the termination of the acid is changed into *ate* : thus the salt formed by the action of nitric acid upon lime is termed calcic *nitrate*, or more strictly, calcic dinitrate ( $Ca_2NO_3$ ). When sulphuric acid acts upon protoxide of iron, the salt produced is called sulphate of iron, or ferrous sulphate ( $FeSO_4$ ) : perchloric acid by its action upon potash furnishes the salt called potassic perchlorate ( $KClO_4$ ). If the name of the acid end in *ous*, the termination is changed to *ite* in naming the salt ; for example, sulphurous acid and baryta by their mutual action form a salt called baric sulphite ( $BaSO_3$ ) : hypochlorous acid and soda by their mutual action form sodic hypochlorite ( $NaClO$ ).

It may here be well to caution those who are just commencing the study of chemistry, of the necessity of distinguishing clearly between compounds such as the sulphites and the sulphates, or the sulphides and the sulphites. Disodic sulphide ( $Na_2S$ ), for example, is a compound, containing a direct product of the combination of two elementary substances, whereas disodic sulphite ( $Na_2SO_3$ ) is a more complex compound formed by the action of two compound bodies upon each other. Disodic sulphate ( $Na_2SO_4$ ), again, contains one proportional more of oxygen than disodic sulphite.

If more than one equivalent of the oxion (or radicle of an

acid) be united with one equivalent of a metal, there is no difficulty in pointing out this fact in the name. A compound of two equivalents of sulphion ( $\text{SO}_4$ ) and two of potassium ( $\text{K}_2\text{SO}_4$ ) would be spoken of as dipotassic sulphate, or sulphate of potassium; but there is another compound of potassium with sulphuric acid, in which two equivalents of the dyad oxion are present to one equivalent of the metal; this compound ( $\text{KHSO}_4$ ) is known as the bisulphate of potash, or more correctly, as hydro-potassic sulphate, or sulphate of potassium and hydrogen; the circumstance of the additional equivalent of acid in this and in other analogous cases being still often conveniently indicated by the prefix *bi* (from the Latin *bis*, twice), or *di* (from the Greek  $\delta\acute{\iota}\varsigma$ ), which is made to precede the name of the acid contained in the neutral salt.

Generally speaking, a metal forms only one basic oxide—that is to say, only one oxide which has the power of forming salts by interaction with acids; but there are several exceptions to this rule. Iron, for example, may form salts corresponding to the protoxide ( $\text{FeO}$ ). Such salts were formerly distinguished as *protosalts*: ( $\text{FeSO}_4 \cdot \text{H}_2\text{O} \cdot 6\text{H}_2\text{O}$ ), represents the composition of the crystallized sulphate of protoxide of iron, often described as protosulphate of iron; but there is another series of salts of iron derived from the peroxide or sesquioxide ( $\text{Fe}_2\text{O}_3$ ) of the metal; these were distinguished as the *persalts*, or *sesquisalts* of iron: ( $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$ ), or ( $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_4$ ), represents the sulphate of the peroxide (or sesquioxide) of iron, and it is frequently termed the persulphate, or sesquisulphate of iron. These terms, although still used, are not free from ambiguity. Berzelius preferred to call the protoxide of iron, *ferrous* oxide, and the protosulphate, ferrous sulphate, whilst the sesquioxide he termed *ferric* oxide, and the sesquisulphate was upon his plan called ferric sulphate. This form of nomenclature unites brevity with precision, and will usually be employed in this work.

Many of these systematic names have an uncouth aspect, and are often long and inharmonious, so that they are frequently abbreviated when the compound spoken of is one of constant recurrence. For example, the sulphates of the alkaline and earthy metals would receive systematic names such as the following:—

$\text{K}_2\text{SO}_4$ , dipotassic sulphate.  
 $\text{KHSO}_4$ , hydropotassic sulphate.  
 $\text{Na}_2\text{SO}_4$ , disodic sulphate.  
 $\text{CaSO}_4$ , calcic sulphate.

It is, however, customary to speak of the normal or neutral



salt of any acid without the numerical prefix; so that, for instance,  $K_2SO_4$  is simply called potassic sulphate, and  $Na_2SO_4$  sodic sulphate, though in reality these names do not indicate their atomic difference from the normal salt of a dyad like calcium, the sulphate of which ( $CaSO_4$ ) is both commonly and correctly spoken of as calcic sulphate.

Again, in the case of the nitrates of the dyad metals, the salts are strictly dinitrates; nitron ( $NO_3$ )' being a monad, for example,

$Ca_2NO_3$ , calcic dinitrate

$Ba_2NO_3$ , baric dinitrate.

Yet we commonly speak of them as calcic nitrate and baric nitrate, and do not in the name indicate the presence of two atoms of nitron; whilst in the sodic salt ( $NaNO_3$ ), which is correctly spoken of as sodic nitrate, only one atom of nitron is present.

Again, in the ordinary or tribasic phosphates, the common lime phosphate ( $Ca_3P_2O_8$ ) should be designated as tricalcic diphosphate, though usually this is abbreviated to calcic phosphate.

When, however, there are many salts of varying composition formed from the same acid, a strict adherence to system is often not only useful, but necessary to avoid confusion. For example, in the three phosphates of soda formed from the ordinary tribasic acid, the proportions of the different basyls require indication:—

$H_3PO_4$ , trihydric phosphate.

$Na_3PO_4$ , trisodic phosphate.

$HNa_2PO_4$ , hydro-disodic phosphate.

$H_2NaPO_4$ , sodic-dihydric phosphate.

Again, it may sometimes be useful to speak of  $Ca_3P_2O_8$  as tricalcic diphosphate; of  $CaH_4P_2O_8$  (superphosphate of lime) as calcic tetrahydric diphosphate; and of  $HNaH_4NPO_4$  (micro-cosmic salt), as ammonio-hydro-sodic phosphate.

By prefixing the numeral in the name to the particular constituent in the salt, whether it be the hydrogen, the sodium, or the oxion, we indicate readily the number of atoms of the particular component which it precedes.

Other forms of nomenclature are applied in particular cases, but these will be best explained as the examples to which they refer arise.

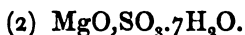
(332) *Empirical and Rational Formulæ*.—In expressing the composition of a body by the use of symbols, the chemist may either content himself with simply stating the result of analysis by a mere enumeration of the elements and the relative number

of proportionals of each, in which case he gives what is termed the *empirical formula* of the body; or he may attempt an explanation of the mode in which he conceives those elements to be associated together, and by the arrangement of his symbols may give expression to a theory of the constitution of the body, and thus assign to it a *rational formula*. A body can have but one empirical formula, but it may be represented by a variety of rational formulæ, according to the different views which may be taken as to the mode in which its components are arranged.

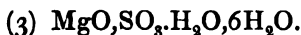
Crystallized magnesian sulphate, for example, has the following empirical formula:—



that is to say, its constituents are present in the ratio of 1 atom of magnesium, 14 of hydrogen, 1 of sulphur, and 11 of oxygen. It is, however, never so written. The water which it contains may be entirely driven off by a heat a little above  $200^{\circ}\text{C}.$ ; and the salt is often represented as consisting of magnesia, sulphuric anhydride, and water, as these are the materials out of which it is formed: thus—



But it is found that at a heat of  $100^{\circ}\text{C}.$ , 6 atoms of the water may be expelled, whilst the seventh atom requires a much higher temperature, so that it appears to occupy a position in the salt different from that of the other 6: this fact may be indicated by slightly altering the second formula, as follows:—



Many chemists, however, guided partly by the results of the electrolysis of the salt, suppose that when once an acid and a base have reacted on each other, their elements are arranged in an order different from that in which they existed when separate, and they prefer to represent the salt accordingly, as



Each of the last three formulæ is a rational formula for magnesian sulphate; and each conveys far more information than the formula No. 1. Each represents a theory founded upon particular modes of decomposition which the salt may be made to experience.

It is impossible that all these formulæ should truly indicate the molecular constitution of the salt, though each may represent the grouping of its component elements under particular circum-

stances. Rational formulæ are indeed indispensable as the exponents of the theories which guide the chemist in his researches, or which aid him in arranging and interpreting phenomena; but, like the theories that they embody, they are only temporary expedients, and they must consequently always be regarded as such, and must be modified or discarded when they no longer faithfully represent the conditions of our knowledge of the compounds which they are employed to indicate. A perfect rational formula would embrace all the modes of decomposition of which a compound is susceptible, and would represent the constitution of the body as well as its various analogies and relations.

(333) *General Arrangement of the Elements adopted in this Work.*—The general division of the elementary bodies into non-metallic and metallic has been already pointed out. There is, however, no strict line of demarkation between the non-metallic and the metallic elements.

The bodies which are considered as non-metallic constitute the electro-negative ingredient in the binary combinations which they form with the metals, and are most of them insulators of the voltaic current. Carbon and silicon, however, in certain forms, act as conductors of electricity. The compounds of the non-metals with oxygen generally show but little tendency to unite with acids; on the contrary, the higher oxides of most of them form compounds which, if acted on by water, furnish powerful acids. These acid-forming oxides, except silica, are readily soluble in water; and even silica, under certain circumstances, may be obtained in solution.

The metals, on the other hand, are characterized by a peculiar combination of opacity and compactness, which gives them, when polished, a peculiar brilliancy, termed the metallic lustre; they are good conductors of heat and electricity, and most of them, by combination with oxygen, form powerful bases. It is, nevertheless, sometimes difficult to determine whether a body should be regarded as a metal or not. Arsenicum has a high metallic lustre; but it is more closely allied to phosphorus than to any other elementary substance, and both its oxides, when dissolved in water, are endowed with well-marked acid properties. Tellurium also exhibits the closest analogy with selenium and with sulphur, but it possesses high lustre, and some conducting power for electricity.

The subdivision of the simple substances into non-metallic and metallic is, however, convenient to the student, and it will therefore be retained in this work. The order in which the different elementary bodies will be treated is not in all cases,

that which a rigid adherence to analogy would indicate, though analogy has guided us, excepting in those instances in which it seemed more advantageous to the student to follow a different course. In most cases we shall first examine the chemical properties which are exhibited by each of the elements in its uncombined form; we shall then study the general nature of its actions upon other elements, and shall afterwards examine the more important compounds into the formation of which it enters.

In describing the properties of the non-metals, it will be found a convenient arrangement to consider first the four elements which enter into the composition of those all-pervading and all-important substances, air and water, and then to pass on to others, classing them together according to the general analogy of their properties. Following this plan, we shall consider first the properties of what may be termed the *atmospheric group* of elements—viz., oxygen; nitrogen (and the atmosphere); hydrogen (and water); carbon (and carbonic anhydride).\*

We shall next examine some of the more important compounds which these bodies form with each other, and shall then describe the well-marked natural group constituting what Berzelius termed the *Halogens*, from the circumstance of their forming with the metals saline compounds resembling common salt; this group comprises chlorine, bromine, iodine, and fluorine.

Three combustible elements will be taken next in order—viz., sulphur, selenium, and tellurium: these will be followed by phosphorus, and the general survey of the non-metallic elements will be completed with silicon and boron.

For the convenience of description and of reference, the metals will be arranged in eight groups, in the following order. The elements which compose each group generally present some natural resemblance, though, as already stated, the classification does not in all cases bring together those which, in chemical habitudes, are really the most closely allied.

#### I. *Alkali-Metals*—5 in number.

1. Potassium.	3. Lithium.	5. Rubidium.
2. Sodium.	4. Cæsium.	

#### II. *Alkaline Earth-Metals*—3 in number.

1. Barium.	2. Strontium.	3. Calcium.
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\* Each of these 4 elements is the representative of one of the 4 principal groups of elementary bodies: hydrogen belongs to the monads; oxygen to the dyads; nitrogen to the triads; while carbon represents the tetrads.

III. *Earth-Metals—8 in number.*

1. Aluminum.	4. Erbium.	7. Lanthanum.
2. Glucinum.	5. Terbium.	8. Didymium.
3. Yttrium.	6. Cerium.	

IV. *Magnesian Metals—3 in number.*

1. Magnesium.	2. Zinc.	3. Cadmium.
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V. *Metals more or less analogous to Iron—6 in number.*

1. Cobalt.	3. Uranium.	5. Chromium.
2. Nickel.	4. Iron.	6. Manganese.

VI. *Metals which yield Acids—12 in number.*

1. Tin.	5. Molybdenum.	9. Vanadium.
2. Titanium.	6. Tungsten.	10. Arsenicum.
3. Zirconium.	7. Niobium.	11. Antimony.
4. Thorium.	8. Tantalum.	12. Bismuth.

VII. *4 Metals.*

1. Copper.	2. Lead.	3. Thallium.	4. Indium.
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VIII. *Noble Metals—9 in number.*

1. Mercury.	4. Platinum.	7. Ruthenium.
2. Silver.	5. Palladium.	8. Osmium.
3. Gold.	6. Rhodium.	9. Iridium.

If a strictly natural order were to be followed in grouping the elements, it would, however, be necessary to modify the foregoing arrangement. This will be rendered evident by pointing out the most important natural groups into which the elementary bodies admit of being subdivided. The detailed indication of the points of resemblance between the members composing each group must be deferred until the properties of the group are considered. In many instances these natural relations between the individual elements thus grouped together are very striking, in others they are more obscurely marked, and in the case of the metals of the earths proper, as well as of the noble metals, the natural chemical relations of these elements with the others are as yet but incompletely known. In the table which follows, the principal elementary bodies are represented in two converging series.

<b>MONADS.</b>		<b>MONADS.</b>	
Fluorine.		Hydrogen.	
Chlorine.		Cæsium.	
Bromine.		Rubidium.	
Iodine.		Potassium.	Silver
<hr/>		Sodium.	Thallium.
<b>DYADS.</b>		Lithium.	
Oxygen.		<hr/>	
Sulphur.		<b>DYADS.</b>	
Selenium.		Barium.	
Tellurium.		Strontium.	
<hr/>		Calcium.	Mercury.
<b>TRIADS.</b>			Copper.
Nitrogen.		Magnesium.	<b>TETRADES.</b>
		Zinc.	Nickel.
		Cadmium.	Cobalt.
		<hr/>	<hr/>
Phosphorus.	Ruthenium.	<b>TETRADES.</b>	
Arsenicum.	Rhodium.	Iron.	
Antimony.	Iridium.	Uranium.	
Bismuth.	Gold.	Cerium.	
<hr/>		<hr/>	
Boron.		<b>HEXADS.</b>	
<hr/>		Chromium.	
<b>TETRADES.</b>		Manganese.	
Carbon.		<hr/>	
	Palladium.	Aluminum.	
Silicon.	Platinum.	<hr/>	
Zirconium.		Molybdenum.	
Thorium.		Tungsten.	
Titanium.	Lead.	<hr/>	
Tin.		<hr/>	

## CHAPTER II.

## A. FIRST DIVISION.—THE NON-METALS.

THE following table gives a general view of some of the most important of the constants of the non-metals. The squares employed in the column headed "Atomic Volume," indicate the relative volumes occupied by a quantity in grammes of each of the different elements, corresponding to the numbers given in the column of "Atomic Weight," assuming that the space occupied by one gramme of hydrogen under similar circumstances of temperature and pressure would fill a space of one square or one volume. One gramme of hydrogen at  $0^{\circ}$  C. and  $760^{\text{mm}}$ . pressure, occupies a space of 11.19 litres.

TABLE OF NON-METALS.

NAME.	Symbol.	Atomic Weight.	Atomic Volume.	Relative wt. H = 1.	Specific gravity.			Fusing point.		Boiling point.	
					Gaseous.			$^{\circ}$ C.	$^{\circ}$ F.	$^{\circ}$ C.	$^{\circ}$ F.
					Theory.	Expt.	Solid.				
Oxygen ...	O	16	<input type="checkbox"/>	16	1.1056	1.1056					
Nitrogen ...	N	14	<input type="checkbox"/>	14	0.9674	0.9713					
Hydrogen...	H	1	<input type="checkbox"/>	1	0.0691	0.0692					
Carbon ...	C	12	<input type="checkbox"/>				3.336	never fused.			
Chlorine ...	Cl	35.5	<input type="checkbox"/>	35.5	2.453	2.47					
Bromine ...	Br	80	<input type="checkbox"/>	80	5.5281	5.54	3.187*	-12.5	9.5	63	145.4
Iodine ...	I	127	<input type="checkbox"/>	127	8.756	8.716	4.947	107	225	175	347
Fluorine ...	F	19	<input type="checkbox"/>	19	1.313						
Sulphur ...	S	32	<input type="checkbox"/>	32	2.2112	2.2	2.05	115	239	446	836
Selenium ...	Se	79.5	<input type="checkbox"/>	79.5	5.486	6.37	4.788	217	423	below redness.	
Tellurium...	Te	129	<input type="checkbox"/>	129	8.913	9.00	6.65	420	800		P
Phosphorus	P	31	<input type="checkbox"/>	62	4.284	4.42	1.83	44	111.5	288	550
Silicon ...	Si	28	<input type="checkbox"/>				2.49		P		
Boron ...	B	10.9	<input type="checkbox"/>				2.68		P		

\* Sp. gr. of liquid at  $0^{\circ}$  C.

## THE ATMOSPHERE. OXYGEN—NITROGEN.

(334) *Compound Nature of the Atmosphere.*—The chemical researches of the philosophers of the last century are especially remarkable on account of the important information which they

afforded upon the nature of the atmosphere. Indeed, the knowledge thus obtained may be regarded as the starting-point of the brilliant chemical discoveries which have since succeeded each other with such rapidity. These researches have abundantly proved that the air is far from being, as it was once supposed to be, an elementary body. It has been found, on the contrary, to be a mixture of several substances, some of which are elementary, others compound.

The most remarkable and abundant of the constituents of the air are the elementary bodies oxygen and nitrogen; and of its compound ingredients, the most important are aqueous vapour and carbonic anhydride.

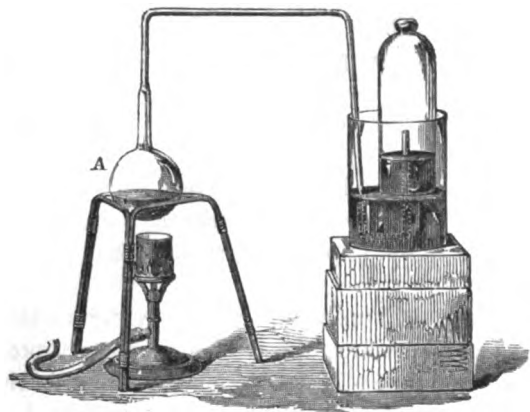
The most direct proofs of the compound character of the atmosphere are afforded by examining the effects produced upon it by burning bodies. Bodies, as is well known, cannot burn without the free access of air. On placing a lighted taper under the receiver of the air-pump and exhausting the air, the flame becomes extinguished. A limited quantity of air will support combustion for but a limited period: a lighted taper floating on water under an inverted bell-glass, the edge of which is plunged beneath the water, soon begins to burn dimly, and at length becomes extinct. But the taper ceases to burn long before the air is all spent; the receiver still contains a large quantity of a gaseous body in which a candle will not burn. The results obtained by burning a candle in a limited portion of air are, however, rather complicated, because the products which are formed by the burning body rise in the form of gas, and become mixed with the remaining portion of air. Lavoisier contrived to obviate this inconvenience by acting upon the air with a substance which produced a solid body as the result of the chemical action, so that it left the air unmixed with any gas which rose from the burning body. The material he employed to decompose the air was metallic mercury, a substance which acts very slowly, and which does not burn in the ordinary sense of the term. The experiment may be performed as follows:—

Into the bulb of a flask or retort (A, fig. 275), provided with a neck of considerable length, an ounce or two of metallic mercury is introduced: the neck of the flask is then bent in the manner shown in the figure, and the bent portion plunged into a mercurial bath, so as to leave the open end of the neck projecting above the level of the mercury, into a jar partially filled with atmospheric air. The bulk of this portion of air is then accurately observed, and the temperature and barometric pressure at the time of the observation are recorded. Heat is now applied to the flask, and maintained steadily at a point just below that required to make the mercury boil. If this temperature be continued for three or four consecutive days, the air inclosed both in the flask and in the jar will



participate in the action. The mercury in the flask will gradually become covered with red scales, and the air, which at first expanded from the action of the heat, and depressed the level of the mercury in the jar, will slowly decrease in bulk, until fresh scales no longer continue to be formed. When this point is reached, the source of heat may be removed, and the remaining air, when cold, will be found to measure about one-fifth less than it did at the commencement. If a portion of this residual air be decanted into

FIG. 275.



another jar, it will be found to be unfit for the support of animal life; a mouse or other small animal introduced into it speedily dies, and the flame of a candle is instantly extinguished. The gas which has been thus obtained is an elementary body, nearly in a state of purity, termed nitrogen (339). In this experiment the heated mercury has been slowly effecting the removal of the oxygen from the air.

§ I. OXYGEN:  $O = 16$ ; *Atomic Vol.*  $\square$ ; *Molecule in free state*,  $OO \square$ ; *Rel. wt.* 16; *Dyad, as in  $H_2O$* ; *Specific Gravity*, 1.1056; \* *not yet liquefied*.

(335) If the red scales which are formed upon mercury when, as in the foregoing experiment, it is heated in a confined portion of air, be introduced into a small glass retort and exposed to a strong heat, they will gradually disappear; drops of

\* Formerly the symbol for oxygen was taken as  $O = 8$ , and the volume occupied by 8 parts by weight of oxygen was employed as the unit of gaseous volume; but the arguments of Gerhardt and the progress of research require that the number for the atomic weight of oxygen should be doubled, if that of hydrogen remains unaltered. Consequently an extensive change in notation, and indeed in the interpretation of chemical phenomena generally, becomes necessary.

If the atomic weight of oxygen be represented as  $O = 16$ , the *molecule* of free oxygen will be  $(OO)$ , with a *molecular weight* = 32, and *molecular volume*  $\square$ ; the atomic weight of hydrogen being ( $H = 1$ ), the molecule of free hydrogen will be  $(HH)$ , occupying the same volume as a molecule of oxygen; and the molecular weight of water will be  $H_2O = 18$ , instead of  $HO = 9$ . In this work the molecular volume of compounds will, unless specifically stated to be otherwise, be represented uniformly by 2 volumes, instead of by the anomalous method of representing some compounds by 2-, others by 4-volume formulæ, as heretofore practised, in the various equations by which chemical reactions are represented.

*Molecular formulæ* will always be employed where it is practicable. Such molecular formulæ will indicate quantities of each compound the volumes of

mercury will become condensed in the cool part of the retort, and a gas will be disengaged, which may be collected over water. If the experiment be performed with accuracy, the quantity of the gas obtained will be exactly equal in volume to the bulk absorbed from the air by the mercury. To this gas the name of *Oxygen* (generator of acids, from  $\acute{o}\xi\acute{\upsilon}\varsigma$  sour, and  $\gamma\epsilon\nu\acute{\alpha}\omega$  to produce) has been given. It is an elementary body, and from the abundance in which it occurs, the number and the variety of its compounds, and the necessary part which it performs in the maintenance of life, it must be regarded as the most remarkable and important of the simple bodies.

*Properties.*—Oxygen possesses extremely powerful chemical attractions for other elementary substances; one element only (fluorine) being known with which it does not combine. Owing to the intensity with which many of these combinations take place, oxygen gas possesses the power of supporting combustion in an eminent degree. If a splinter of wood with a glowing spark on any part of it be plunged into the gas, the wood will instantly burst into flame, and will burn with extraordinary brilliancy. Many bodies which burn tranquilly in air often deflagrate with violence in oxygen.

Phosphorus burns in it with a brilliancy which is painful to the eye; and in like manner sulphur and charcoal, if previously kindled, burn in the gas with great vehemence. Many metals also burn vividly in it; a piece of potassium of the size of a pea, if placed in a small copper spoon, c, fig. 276, and heated strongly by a spirit lamp, bursts into flame when plunged into the

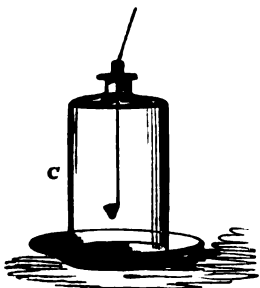
which amount to double the combining volume of hydrogen, if the atom of hydrogen  $H = 1$ ; as for example:—

	Equal vols.	Molecular weight.	Molecular volume.
Free oxygen ... ..	OO	= 32	...
Free hydrogen ... ..	HH	= 2	...
Free chlorine ... ..	ClCl	= 71	...
Free nitrogen ... ..	NN	= 28	...
Hydrochloric acid ... ..	HCl	= 36.5	...
Steam ... ..	H <sub>2</sub> O	= 18	...
Sulphuretted hydrogen ... ..	H <sub>2</sub> S	= 34	...
Seleniuretted hydrogen ... ..	H <sub>2</sub> Se	= 81.5	...

Oxygen belongs to a class of elements including sulphur, selenium, and tellurium, which may be termed *electro-negative dyads*. Each of these bodies is characterized by the power of uniting with twice its volume of hydrogen, furnishing a gaseous compound in which the three volumes are condensed into the space of two: one atom of the elements belonging to this group may be said to be equivalent in combination to two atoms of hydrogen or of one of the halogens. The molecule of these elements contains two atoms: e.g. SS or S<sub>2</sub> = 64, the molecule of sulphur; Se<sub>2</sub> = 159, the molecule of selenium.

gas: if a piece of German tinder be attached to a piece of watch-spring or thin steel wire and be lighted, to start the combustion before it is introduced into the oxygen, the wire will burn with brilliant scintillations; and zinc foil, tipped with sulphur and kindled, burns in oxygen with an intense bluish white light.

FIG. 276.



In all these cases the oxygen combines with the burning body; in each instance a new substance is produced, quite different in properties from either oxygen or the body burned: and when the act of combination ceases the process of burning is at an end.

Oxygen is essential to the support of animal life, and hence by the older chemists was termed *vital air*. A small animal will live in a confined space filled with oxygen for a longer period than in an equal bulk of air; but the gas is of too stimulating a quality to be breathed undiluted with impunity for any considerable time, and before long it produces death from over-excitement of the system.

Oxygen, like air, is destitute of colour, taste, and smell. Of all known substances it exerts the smallest refracting power upon the rays of light. Hitherto all attempts to reduce it to the liquid form by the combined application of pressure and cold have proved fruitless. Oxygen has been proved to possess weak but decided magnetic properties, like those of iron, and like this substance its susceptibility to magnetization is diminished, or even temporarily suspended, by a sufficient elevation of temperature (325). It is heavier than the atmosphere, its specific gravity, according to Regnault, being 1.10563: 1 litre at 0° C., and 760<sup>mm</sup>. pressure, weighing 1.4298 grm.; or 100 cubic inches at 60° F. and 30 inches Bar., weighing 34.203 grains; it is only slightly soluble in water, which takes up about  $\frac{1}{33}$  of its bulk, at 0° C., and  $\frac{1}{33}$  at 15°; 100 volumes of water, according to Bunsen, dissolving 4.11 vols. at 0° C., and 2.99 at 15°.

**Preparation.**—There are several methods of procuring oxygen gas, the simplest of which consist in the exposure of certain metallic oxides to a high temperature, by which they are made to give up, more or less completely, the oxygen with which the metals had combined.

1.—The original method of Priestley, by which he first isolated pure oxygen, in 1774, consisted in heating the red oxide of mercury to about 752° (400° C.),  $2\text{HgO}$  yielding  $2\text{Hg} + \text{O}_2$ ; mercury at a moderate heat having the power of uniting with oxygen, whilst at a somewhat higher temperature the compound is resolved

into its constituents. There are, however, other modes of procuring oxygen which are more convenient and economical.

2.—For the supply of large quantities of oxygen it is usual to employ the black oxide of manganese ( $\text{MnO}_2$ ), a mineral which at a red heat parts with one-third of the oxygen which it contains, whilst a reddish-brown oxide of manganese remains behind;  $3\text{MnO}_2$  giving  $\text{Mn}_3\text{O}_4 + \text{O}_2$ . The mineral must be reduced to small fragments of about the size of a pea, and introduced into an iron bottle, fig. 277, to the neck

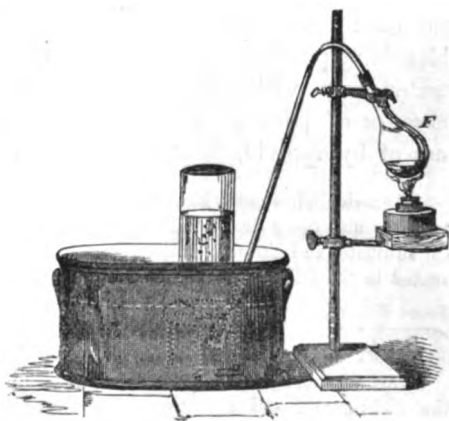
FIG. 277.



of which an iron pipe is fitted by grinding; the bottle is heated in a furnace, and the gas is conveyed to the gas-holder by means of a piece of flexible metallic piping of suitable length. As the oxide of manganese usually contains water as well as a portion of nitrate and some calcic carbonate, the first effect of heat is to drive off a quantity of steam, mixed with a gas which consists principally of carbonic anhydride mixed with nitrogen, which last gas, however, usually is driven off at a later period, and contaminates the oxygen often to the extent of 5 or 6 per cent. When the gas that comes off rekindles a glowing match, it may be collected for use. Black oxide of manganese, when pure, furnishes about one-ninth of its weight of oxygen; but as met with in commerce it seldom yields more than half this quantity, a pound giving off about 1400 cubic inches, or a kilogramme about 50 litres of the gas.

3.—A supply of very pure oxygen may also be obtained readily by the action of heat upon the salt known as chlorate of potash, or potassic chlorate. About

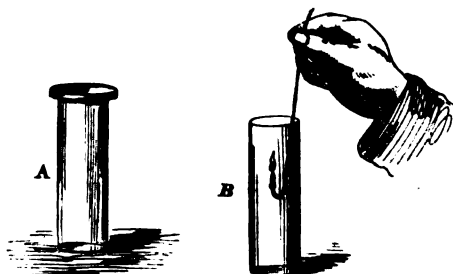
FIG. 278.



half an ounce, or from 15 to 20 grammes of this salt may be heated over a gas flame or a charcoal fire, in a green glass retort, or in a Florence flask, *F* (fig. 278), furnished with a cork which is adapted to a bent tube for delivering the gas: the salt fuses at a heat below redness, and at a temperature a little above its melting point emits a large quantity of gas, which may be collected in jars over water in the pneumatic trough, or it may, if not wanted for immediate use, be stored up in a gas-holder (39). If a jar of the gas be closed with a glass plate it may readily be inverted, as at *A*, fig. 279, and its power of supporting combustion tested by a taper, as shown at *B*. The oxygen furnished by the chlorate amounts to more than one-third of the weight of the salt used; 1 ounce or 28.3 grms. of the crystals should yield about 9 litres, or nearly 2 gallons of the gas. Potassic chlorate ( $\text{KClO}_3$ ), is a compound of chlorion ( $\text{ClO}_3$ ) with potassium; when heated sufficiently, the salt is decomposed, and gives up all its oxygen in the gaseous form, whilst the chlorine and potassium unite, and constitute the white salt which remains in

the retort when the operation is over. The change may be thus represented in symbols:  $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$ .

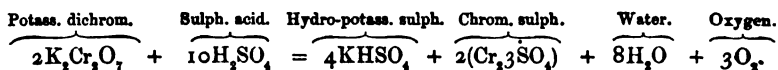
FIG. 279.



4.—When the quantities of chlorate employed are rather large, the heat required is apt to soften the glass of the flask in which it is decomposed. It has, however, been found that many metallic oxides, if mixed in fine powder with the pulverized chlorate in a proportion of not less than one part to ten of the salt, cause the expulsion of the gas at a much lower temperature, ranging between  $450^\circ$  and  $500^\circ$  F. ( $232^\circ$  and  $260^\circ$  C.), although such oxides have not been proved to experience any chemical change during the operation (1008). It is therefore convenient in practice to mix potassic chlorate with about a fourth of its weight of black oxide of copper ( $\text{CuO}$ ) or of oxide of manganese, that has been previously heated to redness and allowed to cool. The gas which is obtained in this way always contains traces of chlorine, and the heat must be carefully watched, as at a particular point the oxygen is disengaged with very great rapidity.

Oxygen may be obtained from various other substances, but those already mentioned are the best, and are the materials most frequently employed. Red lead, and the peroxides of most of the metals, such as those of silver and lead, as well as the nitrates of potassium, sodium, and barium, when heated strongly, furnish the gas; it may also be obtained by heating chloride of lime or bleaching powder; and a mixture of sulphuric acid in its concentrated form, with half its weight of powdered oxide of manganese, or of potassic dichromate ( $\text{K}_2\text{CrO}_4\text{CrO}_3$ ) may also be made use of by applying heat to the materials placed in a glass retort.

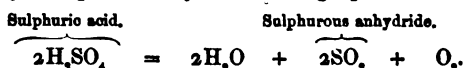
Potassic dichromate (bichromate of potash) and sulphuric acid when heated together undergo a decomposition, in consequence of which, oxygen, hydro-potassic sulphate, and chromic sulphate are produced. This change may be represented in the following manner:—



Part of the sulphuric acid is employed in displacing the chromic acid from the dichromate, and in forming hydro-potassic sulphate in its stead, whilst another portion of the sulphuric acid assists in decomposing the liberated chromic acid, which loses half its oxygen, and becomes converted into chromic oxide; and the chromium of this oxide, by exchanging places with the hydrogen of the sulphuric acid, forms chromic sulphate, whilst water is formed.

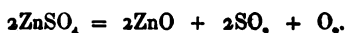
When oxygen is required in large quantities, as in metallurgic operations, Deville and Debray recommend the decomposition of sulphuric acid by heat as the cheapest source of the gas. A tubulated earthenware retort is charged with fragments of fire-brick, an iron tube sufficiently long to reach to the bottom of the retort is luted into the tubulure, and when the retort is at a full red heat,

the acid is allowed to pass in, drop by drop, through a bent funnel. In this operation the sulphuric acid is decomposed into sulphurous anhydride, oxygen, and water, as may be represented by the following equation:—



The volatilized products are transmitted through a small spiral condenser to liquefy the water and undecomposed acid, whilst the sulphurous anhydride is removed by subsequent washing with water, and the oxygen is collected in the usual manner.

Dried zincic sulphate likewise furnishes oxygen and sulphurous anhydride readily on the application of a full red heat, while zincic oxide remains in the retort:—



Baric dioxide,  $\text{BaO}_2$ , was also proposed by Bous-singault as a source of oxygen. He hoped alternately to convert baryta into the dioxide, by heating it to dull redness in a current of air, and then to decompose the dioxide by a still more elevated temperature, and thus to be able to extract oxygen from the atmosphere with the same quantity of baryta for an indefinite number of times, but hitherto the difficulties attending the use of this method have prevented its application in the arts.

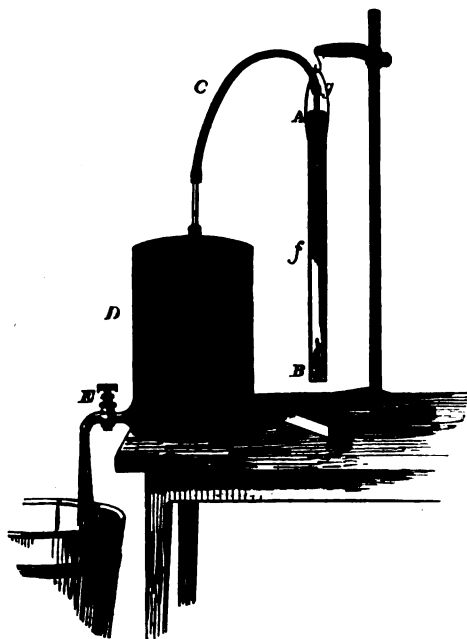
(336) *Nature of Combustion.*—The distinguishing feature of oxygen is its remarkable power of supporting combustion. Whenever any rapid chemical action attended with extrication of light and heat takes place, *combustion* is said to occur. In order to commence this action it is generally necessary to apply heat; afterwards the heat which is liberated during the process is more than sufficient to carry it on, and the act of combination proceeds with increasing rapidity. A stick of charcoal may be kept in oxygen at common temperatures for years without entering into combination with the gas, but the smallest spark upon the surface of the charcoal will suffice to determine its immediate and vivid combustion.

It must ever be borne in mind that in the case of combustion, as in every instance of chemical action, how completely soever the combustible, or body which is burned, may change its form, so as even to disappear from our sight, there is no actual destruction of matter or loss of weight. A candle in burning seems to be completely destroyed; and when the combustion is over, an insignificant trace of ash from the wick is all that remains to the eye. It is, however, easy to show that there is no actual destruction of its components in this operation, but that the constituents of the candle in burning have combined with a certain proportion of oxygen, and that the æriform compounds, carbonic anhydride and aqueous vapour, which are the result of the combustion, though invisible, really weigh more than the

original candle; the gain in weight representing the quantity of oxygen which has produced the chemical change by its combination with the materials of the candle.

The experiment may be conducted in the following manner:—Take a glass

FIG. 280.



tube, A B, fig. 280, 14 or 15 inches (35 or 40 centimetres) long, and  $1\frac{1}{2}$  inch (or 4 centimetres) in diameter; thrust a piece of wire gauze, *f*, half way down the tube, and fill the upper half with fragments of fused caustic potash. The fused potash is employed to retain both the carbonic anhydride and the moisture, which are the only compounds produced by the burning candle, if it be properly supplied with air. To the lower end of the tube fit a cork perforated with three or four holes for the admission of air, and fasten to it a short piece of wax taper. To the other end of the tube adapt a cork, through which a short piece of tube, *g*, of about one-third of an inch (8<sup>mm</sup>.) in diameter is passed. Now weigh the tube and its contents. Connect the tube *g* by means of a piece of flexible tubing, *c*, to an aspirator jar,

*D*, filled with water; open the stopcock, *E*, and let the water flow. The water cannot escape at *E* till its place is supplied by atmospheric air; and since the aspirator, through the tube *c*, is connected with A B, which at *B* communicates freely with the atmosphere, a current of air is established through A B. Now withdraw the cork *B*, light the taper, and quickly replace it in the tube; in about three minutes' time close the stopcock of the aspirator; the taper is instantly extinguished. Detach the tube *c*; the glass A B, when cold, will weigh several decigrammes heavier than before.

At the ordinary temperature of the atmosphere oxygen frequently enters slowly into combination without any perceptible disengagement of heat, as when a bar of iron is gradually rusting in the air.\* In other instances, where the process is more rapid,

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\* When considerable masses of iron are allowed to rust, a distinct elevation of temperature is often perceived. This is seen when a heap of iron turnings of from 11 to 22 lb. (5 to 10 kilog.) is moistened with water and exposed to the air; and a curious illustration of the fact was afforded during the manufacture of the Mediterranean electric cable. The copper conducting wire of this cable was

the heat accumulates, and sometimes it rises high enough to cause the materials to burst into flame, producing what are called cases of spontaneous combustion. Charcoal that has been reduced to fine powder as a preliminary to the manufacture of gunpowder, and which offers a large surface to the air, occasionally exhibits this phenomenon; and it is still more often manifested when tow that has been used for wiping machinery lubricated with oil is laid aside in heaps. The oil, when spread over so large a surface, absorbs oxygen rapidly, and the temperature goes on rising until the mass bursts into flame.

The oxidation of the metals has been observed to take place much more rapidly in a moist than in a dry atmosphere. A bar of polished iron will remain in dry air unchanged for any length of time, but if moisture be present it will quickly become rusty; the oxide of iron in this case combines with the water which it absorbs from the air (753). In the case of iron, the oxidation continues to spread through the entire mass of the metal; but in other instances, as occurs with lead and zinc, a superficial coat of oxide is formed, which adheres firmly to the surface, and protects the metal beneath from further change.

The more the oxygen is diluted, whether by diminution of pressure, or by mixture with a gas which does not act chemically upon it, as with the nitrogen of the atmosphere, the less elevated is the temperature which is produced in a given time by combustion, because fewer particles are in contact with the burning body, whilst at the same time the diluting gas must have its temperature raised, and the more slowly, in consequence, does the operation proceed. The activity of the combustion is greatly

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coated with gutta-percha, this was covered with a serving of tar and hemp, and the whole was enclosed in a strong casing of iron wire. The cable as it was manufactured was coiled in tanks filled with water. These tanks leaked, and the water was in consequence drawn off, leaving a quantity of cable, about 163 nautical miles in length, coiled into a mass about 30 feet or 9 metres in diameter, with an eye or central space of 6 feet, (rather less than 2 metres); the height of the coil was about 8 feet (2·5 metres). Rapid oxidation took place, and the temperature at the centre of the coil, nearly 3 feet (0·9 metre) from the bottom, rose in 4 days from 66° to 79° (19° to 26° C.), although the temperature of the air did not exceed 66° (19° C.), during the period, and was as low as 59° (15° C.) part of the time. In other parts of the mass the heat rose so high as to cause the water to evaporate sufficiently rapidly to produce a visible cloud of vapour, and to give rise to apprehensions that the insulating power of the cable would be destroyed by the softening of the gutta-percha. No doubt the rise of temperature would have been still greater had it not been checked by the affusion of cold water; but the oxidation and the heating were renewed when the affusion was discontinued. The oxidation occurred only on the external surface of the iron wires, that portion in contact with the tarred hemp remaining perfectly bright.



augmented by increasing the number of particles of oxygen which are brought in a given time into contact with the combustible, as well as by carrying away the gaseous products of combustion which are incapable of combining with the fuel, and which, if suffered to accumulate, would cut off the supply of fresh oxygen; in this way the action of the smith's bellows and the blowing machine of the blast furnace may be explained. The influence of a long chimney in producing a powerful heat in the furnace at its base is similar; whilst the effect of diminishing the supply of air by closing the damper, or shutting the door of the ash-pit, is seen in the diminished temperature and reduced consumption of fuel which occur under such circumstances.

It is, however, important to remark that the quantity of heat emitted during the combination of a given quantity of oxygen is definite, and is dependent in part upon the chemical nature of the burning body, but it is independent of the rate at which the combustion is effected (199 *et seq.*).

The act of respiration in animals, during which the oxygen of the air is brought into contact with the blood through the agency of the lungs, is attended with a slow change, analogous to combustion, and is accompanied by extrication of heat; an oxidation of a portion of the constituents of the blood occurs, carbonic anhydride is extricated and passes off with the expired air, and at the same time the colour of the blood is changed from a dusky purple to bright crimson.

All bodies may, with reference to combustion, be arranged under one of three classes. The first class consists of bodies which, like oxygen, allow other substances to burn in them freely, but which cannot themselves, in ordinary language, be set on fire: these are termed *supporters of combustion*. The second class consists of bodies which, like charcoal, actually burn when sufficiently heated in a gas belonging to the first class: these substances are termed *combustibles*. The third class embraces such bodies as will neither burn themselves nor support the combustion of others: they may be made red hot, but do not burn; sand, iron-rust, and earthy bodies in general, afford examples of this kind; they are for the most part compounds that have at some time or other been produced by combustion; that is, they are bodies that have been already burned, and are no longer fitted to undergo this change.

(337) *Varieties of Oxides*.—The compounds which oxygen forms with other elements are in chemical language termed *oxides*, and a body which has combined with oxygen is said to have

become *oxidized*. The number and variety of these compounds are very great, for oxygen is the most widely diffused and abundant of the elements. It constitutes about a fifth in bulk of the atmosphere; it forms eight-ninths of all the water on the globe, and it is not less extensively met with amongst the solid constituents of the earth: chalk, limestone, and marble—silica, in all its varieties of sand, flint, quartz, rock-crystal, &c.—and all the various kinds of clay, each contain about half their weight of oxygen. In the forms of animal and vegetable life it is also equally generally diffused; it is indeed absolutely essential to the maintenance of the vital functions in both; and although not the only body which is fitted to support combustion, it is, from its existence in the atmosphere, the element which, in the vast majority of cases, maintains combustion on the surface of our planet.

Amongst the various compounds formed by oxygen, it is remarkable that there exist two classes which are in chemical properties directly opposed to each other. Many substances, like phosphorus, by their combination with oxygen, yield a compound which is freely soluble in water, has a sour, burning taste, and turns many vegetable blue colours, such as the blue of an infusion of litmus or of purple cabbage, to a bright red, and which, in short, possesses the characters of an *acid*. All the elements which are not metallic, with the exception of hydrogen and fluorine, form with oxygen one or more compounds, which, when dissolved in water, are acids, and in many cases intensely powerful acids. Many of the metals, however, by their union with oxygen, give rise to bodies of an opposite kind, which have been termed *bases*. Potassium, for example, when burned in oxygen, furnishes a white alkaline substance, which is dissolved rapidly by water, and produces a colourless liquid, of a soapy, disagreeable taste, and a peculiar lixivial smell: it has a caustic action on the skin, restores the blue colour to litmus which has been reddened by an acid, and it completely neutralizes the strongest acids. Other metals form oxides which, though not soluble in water, nevertheless preserve their basic character, and neutralize the acids perfectly. Ferrous oxide, for instance, is soluble in sulphuric acid, and forms with it a crystallizable salt, whilst water is set free. It is found in almost all cases that when an element combines with oxygen to form an acid, it unites with a larger number of atoms of oxygen than when a base is the result of the combination.

Intermediate between the acid and the basic oxides is a third

class of oxides, which are indisposed to enter into combination with either acids or bases. The black oxide of manganese ( $\text{MnO}_2$ ), or ( $\text{MnO}, \text{MnO}_2$ ), the magnetic oxide of iron ( $\text{FeO}, \text{Fe}_2\text{O}_3$ ), and red lead ( $2\text{PbO}, \text{PbO}_2$ ), may be mentioned as instances of this kind: such oxides are often produced by the union of two other oxides with each other. These indifferent oxides are sometimes termed *saline* oxides, from their analogy to salts in composition (547 *et seq.*).

Independently of its power of supporting animal life and combustion, oxygen may be distinguished by direct tests. It is insoluble in a solution of potash, but if to the alkaline liquid a little pyrogallic acid be added, the gas is rapidly absorbed, and the solution becomes of an intense brown colour. A mixture of nitric oxide with any gas containing uncombined oxygen immediately becomes of a reddish-brown colour, owing to the formation of red fumes of peroxide of nitrogen (365, 567): and a colourless solution of cupreous oxide in ammonia instantly becomes blue by absorbing oxygen when exposed to any mixture containing uncombined oxygen (875).

(338) OZONE.—When a succession of electric sparks is transmitted through atmospheric air or through dry oxygen, a peculiar odour is perceived, which has by some been compared to that of weak chlorine. To the body which produces it Schönbein gave the name of *ozone* (from  $\text{o}\zeta\omega$ , to emit an odour) in allusion to its strong and peculiar odour. Opinions upon the cause of this odour were long divided; but the concurrent observations of several accurate experimentalists seem to indicate that it is owing to a modification produced in oxygen itself, by which it is made to assume a more active condition. One of the easiest methods of exhibiting the production of ozone consists in transmitting a current of oxygen through a tube into which a pair of platinum wires is sealed, with the points at a little distance apart: on connecting one of the wires with the prime conductor of an electrical machine in good action, whilst the other wire is in conducting communication with the earth, the characteristic odour of ozone is immediately developed in the issuing gas; but notwithstanding the powerful odour thus produced, a minute portion only of the oxygen undergoes this change. Andrews and Tait (*Phil. Trans.* 1860) have shown that in order to produce the maximum effect in electrifying oxygen, it is necessary to transmit the discharge *silently*. By operating in sealed tubes upon pure and dry oxygen, they succeeded, when great care was taken to prevent the transmission of sparks, in converting a large portion of the gas into

ozone. Ozone is much denser than oxygen itself; by a continuous electrical discharge maintained for many hours, they effected a contraction in bulk of the gas amounting to one-twelfth of the entire volume operated on; and on heating the gas to  $550^{\circ}$  ( $288^{\circ}$  C.) the ozone disappeared, whilst the oxygen resumed its original volume. The passage of the electric *spark* likewise immediately destroys a large proportion of the ozone which had been previously produced.

Siemens prepares ozone by induction: he forms a sort of Leyden jar by coating the interior of a long tube with tinfoil: over this tube he passes a second wider tube also coated with tinfoil, but on its outer surface; he then transmits between the two tubes a current of pure dry oxygen, which becomes electrified by induction, on connecting the inner and outer coating with the terminal wires of an induction-coil.

Ozone may also be obtained without the aid of electricity. Houzeau states that the oxygen evolved from baric dioxide ( $\text{BaO}_2$ ) by the addition of oil of vitriol, contains ozone; it has a powerful odour, and he found that it oxidizes ammonia, and kindles the less inflammable variety of phosphuretted hydrogen (454); after it has been heated it no longer possesses these properties. Later researches have, however, rendered it probable that these properties are due to the formation of peroxide of hydrogen in small quantity, and to its suspension in the oxygen as it escapes.\*

If a stick of clean phosphorus, moistened with a few drops of water, be placed in a bottle of atmospheric air, at a temperature of from  $60^{\circ}$  to  $70^{\circ}$  ( $15^{\circ}$  to  $21^{\circ}$  C.), the slow oxidation of the phosphorus is attended with the production of ozone: in an hour or two this attains its maximum. If the phosphorus be not then removed, the ozone by degrees disappears, owing to its combination with the phosphorus. No ozone is formed if the air be perfectly dry; and dry

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\* The reader is referred for Schönbein's speculations upon the existence of two opposite forms of oxygen, ozone and antozone, to the *Phil. Mag.* for 1858. They are ingenious, but although the existence of two oppositely polarized forms had previously been rendered probable by the experiments of Brodie and others, it is not in accordance with analogy, that ozone should be the isolated form of one of these bodies. A mixture of a solution of potassic permanganate with one of peroxide of hydrogen evolves oxygen, whilst hydrated peroxide of manganese is precipitated; and in like manner a solution of chromic acid acidulated with sulphuric acid gives off oxygen on the addition of peroxide of hydrogen, whilst green chromic sulphate is produced. Hence it has been supposed that the oxygen in the permanganic or chromic acid is in an opposite polar condition to the second atom of oxygen in the peroxide of hydrogen; the tendency to union between these two supposed oppositely polar forms of oxygen is conceived to be the cause of the decomposition, and the result of their union is the gaseous oxygen which escapes. (See also Brodie, *Phil. Trans.* 1850 and 1862.) Von Babo's experiments tend to show that Schönbein's so-called antozone is peroxide of hydrogen. The subject, however, still needs further investigation.

oxygen is not ozonized by phosphorus. It is also probable that ozone is formed in other slow oxidations, such as that of ether, and of oil of turpentine. Schönbein appears to have proved that in all such cases the formation of ozone is accompanied by that of peroxide of hydrogen ( $H_2O_2$ ), a fact which is true also of electrolytic ozone.\* Ozone, as obtained by any of these processes, is present in but very minute quantity, being diluted with from 50 to 200 times its volume of oxygen.

When diluted sulphuric acid, or a solution of the sulphates, chromates, phosphates, and several other salts of the alkali-metals, is decomposed electrolytically between plates of platinum or gold by the voltaic battery, the oxygen that is evolved has a powerful odour of ozone. The experiments of Andrews (*Phil. Trans.* 1855 and 1860) have shown the identity of the ozone obtained by the electricity of the machine, with that produced by voltaic action, as well as with that obtained by the oxidation of phosphorus; and these conclusions have been confirmed by Soret and by Von Babo (*Liebig's Annal., Suppl.-bd.*, ii. 266), in opposition to Baumert, who maintained (*Pogg. Annal.* lxxxix. 38) that electrolytic ozone contains a peculiar peroxide of hydrogen, as Schönbein himself at one time supposed.

*Properties.*—Ozone is insoluble in water, and in solutions either of acids or alkalis, but is absorbed by a solution of potassic iodide. Air charged with ozone exerts an irritating action upon the respiratory organs. Ozone possesses considerable bleaching powers, and converts blue indigo into isatin: it acts rapidly as a powerful oxidizing agent, and corrodes organic matters, such as the cork or caoutchouc used in connecting the different parts of the apparatus together: iron, copper, and even silver, when moistened, absorb it rapidly, and become converted on their surface into oxides: silver even becomes a peroxide, though this metal does not enter into direct combination with ordinary oxygen either when moist or dry. When the ozone and the metals are perfectly dry, little or no absorption of ozone occurs. Dry mercury, however, as well as dry iodine immediately removes ozone. It is remarkable that no contraction follows the absorption of ozone by these or by any other agents; this point was carefully and minutely observed by

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\* If a clean glass rod heated to about  $500^{\circ}$  ( $260^{\circ}$  C.), be plunged into a jar containing a few drops of ether, the vapour of ether undergoes slow oxidation, and ozone seems to be formed: the vapours turn starch paper, moistened with a solution of potassic iodide, blue; the residual ether contains peroxide of hydrogen, and if agitated with a few drops of a solution of potassic chromate acidulated with a little sulphuric acid, a blue solution of perchromic acid in the ether is produced.

Andrews and Tait. Hence it seems to be probable that the ozone is resolved into a quantity of ordinary oxygen, equal in bulk to itself, which is liberated at the moment that another portion of oxygen enters into combination with the iodine; possibly three volumes of oxygen become condensed into two; one volume becoming fixed, whilst two volumes are liberated on the decomposition of ozone by a metal. Some experiments by Soret favour this supposition; but the quantity of ozone operated on is so small compared with the bulk of air with which it is diluted, that the measures obtained are not very trustworthy. Ozone displaces iodine from its combinations with the metals, setting the iodine at liberty; indeed, this reaction is so easily produced, that it furnishes the readiest and most delicate method of detecting the presence of traces of ozone in the air; a slip of paper moistened with starch and potassic iodide, and inserted into a vessel containing the smallest admixture of ozone, becomes blue from the action of the liberated iodine, which immediately unites with the starch, and forms the blue iodide of starch which is so characteristic of iodine. Indeed, pure oxygen contained in a tube inverted over a solution of potassic iodide is entirely absorbed by the liquid, if the gas be subjected to the passage of a discharge of electricity through it for a sufficient length of time, potassic hydrate being formed by the absorption of oxygen, while iodine is set free:  $(4KI + 2H_2O + O_3 = 4KHO + 2I_2)$ . If the experiment be prolonged, potassic iodate, peroxide of hydrogen and peroxide of potassium are formed. Paper soaked in a solution of manganous sulphate ( $MnSO_4$ ) likewise shows the presence of ozone by becoming brown, owing to the manganese in the sulphate absorbing oxygen, and becoming converted into the insoluble hydrated peroxide, whilst sulphuric acid is set free. If the paper be stained black with plumbic sulphide ( $PbS$ ), this stain will gradually disappear; both the sulphur and the lead will absorb the ozone, or active oxygen, and white plumbic sulphate ( $PbSO_4$ ) will be formed. One of the most singular circumstances connected with ozone is the effect of heat upon it. A temperature not much higher than that of boiling water is sufficient slowly to destroy all its active character, and the change is instantaneous at the temperature of  $572^\circ$  ( $300^\circ C.$ ). By placing the flame of a spirit-lamp so as to heat a part of the tube through which the electrified oxygen escapes, all signs of ozone disappear. Ozonized air is also deozonized by transmission over cold manganic dioxide, argentic dioxide, or plumbic dioxide.

If a piece of paper, soaked in a mixture of starch and potassic

iodide be exposed in the open air for five or ten minutes, it often acquires a blue tint, the intensity of which varies on different days; sometimes, particularly in damp or foggy weather, no change is produced by such exposure. These effects are seldom seen in towns, but generally in the open country, or on the sea coast, especially when the wind blows off the sea. They are plausibly supposed to be owing to the presence of traces of ozone in the atmosphere; and theorists are not wanting who believe they have traced the prevalence of cholera and other epidemics to the unusual absence of ozone in the air during lengthened periods. Iodine may, however, be liberated from potassic iodide by nitrous acid, by chlorine, and by various agents besides ozone, so that this reaction, although a very sensitive one for ozone, is by no means characteristic of its presence; and the existence of traces of ozone in the atmosphere, probable though it is, cannot be said to have been unequivocally proved; although some agent more powerful in its oxidizing actions than ordinary oxygen is present in variable amount. Schönbein, in order to obtain some idea of the proportion of the agent which produces the effect, prepares the test-paper of a definite strength, by dissolving 1 part of pure potassic iodide free from iodate in 200 parts of distilled water, which is thickened by heating it with 10 parts of white starch: this is then spread upon slips of unsized paper, which are preserved in a stoppered bottle kept in the dark.

Daubeny (*J. Chem. Soc.* 1867, 19) appears to have proved distinctly that most plants, when growing in the sunshine, produce a minute quantity of an agent which liberates iodine from potassic iodide: and he seems also to have demonstrated the absence of chlorine and of nitrous acid in these experiments.

## § II. NITROGEN.\* $N=14$ .

*Atomic Vol.*  $\square$ ; *Rel. wt.* 14; *Theoretic Sp. Gr.* 0.9674; *Observed Sp. Gr.* 0.9713; *usually Triad, as in  $H_3N$ , sometimes Pentad.*

(339) It has already been stated (334) that the larger proportion of the atmosphere consists of a gaseous body, which has been named *nitrogen* (generator of nitre), because it is an essential constituent of nitre: sometimes the name of *azote* (from  $\alpha$  not,  $\zeta\omega\eta$  life,) is given to it, because, though not poisonous, it is incapable of supporting life. This element was discovered by Rutherford in 1772.

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\* If nitrogen in the gaseous state be regarded as (NN) *nitride of nitrogen*, its *molecular* volume will be  $\square\square$ , and its *molecular* weight = 28.

*Properties.*—Nitrogen is a colourless, tasteless, and inodorous gas, which as yet has resisted every effort to liquefy it. It is somewhat lighter than atmospheric air; from Regnault's experiments, 1 litre at  $0^{\circ}$  C. and 760<sup>mm</sup>. pressure weighs 1.256167 gramme, or 100 cubic inches at  $60^{\circ}$  F., Bar., 30 inches, weigh 30.119 grains. Water dissolves not more than a thirtieth of its bulk of this gas at ordinary temperatures, 100 volumes of water at  $0^{\circ}$  C. absorbing 2.03 vols. of nitrogen, and 1.48 vols. at  $15^{\circ}$  (Bunsen). No two substances can offer a more striking contrast in chemical properties than oxygen and nitrogen: the one the most energetic of the elements, the other the most indifferent. It extinguishes a taper without taking fire itself: an animal immersed in the undiluted gas perishes quickly for want of oxygen, but it is not directly poisonous; indeed, it enters as a necessary component into the animal frame, and with every act of inspiration it finds admission into the lungs. One very important purpose that it fulfils in the atmosphere is the dilution of the oxygen, which is rendered thereby less stimulating to the living system, and the rapidity of ordinary combustion is likewise thereby moderated. Nitrogen is one of the most extensively diffused forms of matter, as must be evident from the facts just stated; and notwithstanding its apparent indisposition to enter into combination, it forms a number of highly interesting and important compounds. For example, one of its combinations with oxygen, when dissolved in water, forms nitric acid, which exists as a natural production when united with potassium and sodium in the nitrates of those metals: it is the characteristic ingredient in ammonia; and though it occurs in but small quantity in plants, it is never entirely absent from them. Nitrogen also constitutes an essential part of many of the most potent and valuable medicines, such as quinia and morphia, as well as of some of the most dangerous poisons, as prussic acid and strychnia. It likewise enters largely into the composition of many animal tissues. Organic compounds which contain nitrogen are frequently termed *azotized* substances.

*Preparation.*—The most convenient methods of obtaining nitrogen are based upon the removal of oxygen from atmospheric air. 1.—The simplest plan consists in placing a few fragments of phosphorus, dried by means of blotting-paper, on a porcelain dish which is floated upon the surface of the water of the pneumatic trough; the phosphorus is ignited by touching it with a hot wire, and a glass receiver filled with air is then inverted over it. The phosphorus burns at the expense of the oxygen in the



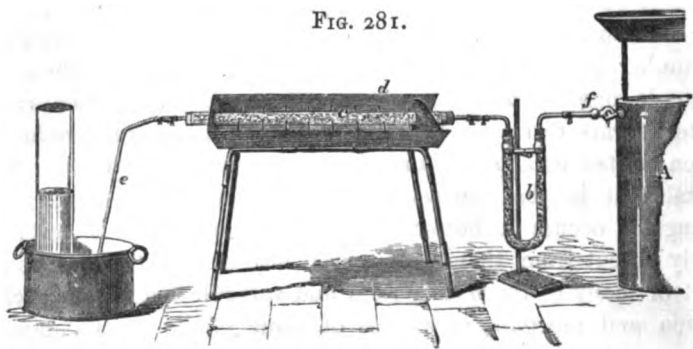
confined air, and being partially converted into vapour by the heat which attends the combustion, is diffused through the gas, and thus quickly searches out and combines with every portion of oxygen: when cold, the nitrogen may be decanted into another jar and examined. Even at ordinary temperatures, a stick of phosphorus will, if introduced into a jar of air which is standing over water, slowly absorb the oxygen, and in two or three days about four-fifths of the original bulk of the air, consisting of nitrogen nearly pure, will be left.

2.—The removal of oxygen from the air may also be effected slowly in various ways. Moistened iron filings may be used for this purpose, the metal gradually becoming oxidized, as is seen by the rusty appearance which it assumes. Many other metals, when moist, as, for example, moistened lead shavings, produce a similar effect.

3.—Moistened sulphides of the alkaline metals likewise absorb oxygen from a confined portion of air very rapidly and completely.

4.—When larger quantities of nitrogen are required, metallic copper may be employed to remove the oxygen. The method to be adopted in this case is exhibited in fig. 281:—*c* represents a long straight tube of hard glass, which will

FIG. 281.



resist a strong heat without fusion: it is filled with metallic copper in a finely divided state; for this purpose the metal which has been reduced from the powdered oxide by means of hydrogen gas is well adapted. The tube *c* rests on a sheet-iron furnace, *d*, in which it can be surrounded by charcoal and raised to a red heat; *e* is a bent tube for delivering the gas into a jar over water or mercury; the other extremity of the tube *c* is connected with a bent tube, *b*, filled with fragments of fused caustic potash; and the air which supplies the nitrogen is driven from the gas-holder, *A*, over the ignited copper in a stream which is easily regulated by the stopcock, *f*. The air first traverses the tube which contains the fused potash, where it leaves all traces of carbonic anhydride and moisture, and it then passes over the ignited copper, by which every portion of oxygen is completely removed.

5 and 6.—Nitrogen may also be obtained by the action of

chlorine on a solution of ammonia (386), and it is furnished in a state of purity by heating a solution of ammoniac nitrite (369). De Luna obtains it by heating in a flask equal weights of potassic dichromate and sal ammoniac, which must be finely powdered, and intimately mixed. (*Note*, par. 369.)

### § III. COMPOSITION OF THE ATMOSPHERE.

(340) IF a mixture be made of 4 measures of nitrogen and 1 measure of oxygen gas, a candle will burn in it as in atmospheric air; it may be breathed as air, and possesses the ordinary properties of the air. The atmosphere is, in short, a mechanical mixture of several gases, amongst which oxygen and nitrogen constitute the principal portions: these gases, notwithstanding their difference in density, are, owing to the principle of diffusion (67), uniformly mixed with each other. Chemical operations are continually occurring upon the earth's surface, which remove oxygen and add a variety of other gases, amongst which carbonic anhydride is most abundant. Yet so wonderfully adjusted is the balance of chemical actions over the face of the earth, that no perceptible change in the composition of the atmosphere has been observed since accurate experiments on the subject have been practised.

Air which has been freed from carbonic anhydride and aqueous vapour consists, according to the numerous careful analyses of Dumas and Boussingault (*Ann. de Chimie*, III. iii. 257), on an average of 20·81 of oxygen by measure, and 79·19 of nitrogen in 100·00 vols.; or by weight of 23·01 of oxygen, and 76·99 of nitrogen. These experiments were performed by allowing the air to stream slowly over a weighed quantity of heated copper, by which the oxygen was absorbed (fig. 281) whilst the nitrogen was received into an exhausted flask, which was weighed before the experiment was commenced and after its termination; the quantity of oxygen was found by the gain in weight experienced by the tube containing the copper. The results obtained by Regnault, Brunner, Verver, and others, by different methods of analysis, do not vary more than  $\frac{1}{500}$  from the quantity of oxygen just mentioned. Trifling temporary variations no doubt occur from local causes; but the air brought by Gay-Lussac from an elevation of four miles above the surface of the earth, that collected on the summit of the Alps, and that examined both in town and country in various parts of the globe, presents no sensible difference from the mean above given.

A portion of air collected by Mr. Welsh, in August, 1852, at an elevation

of 5486 metres, or 18,000 feet, in one of the balloon ascents undertaken by him and Mr. Green under the direction of the Kew Committee of the British Association, contained 20·88 per cent. of oxygen by volume, while air collected at the surface at the same time contained 20·92. The air was collected in tubes of about 6 cub. in., or 100 cub. centim. in capacity, fitted with accurate stopcocks. They were exhausted previously to the ascent, and were filled with the air for examination by opening the stopcocks, which were again closed as soon as the charge had entered. In the extensive series of experiments of Regnault (*Ann. de Chimie*, III. xxxvi., 385), air was collected at different points of the earth's surface in glass tubes, drawn out to an open capillary extremity at either end, fig. 282. When a specimen of air was to be collected, one of these tubes was

FIG. 282.



attached by a flexible tube to a small pair of bellows, and by working the bellows a few times, the tube was filled with air of the locality. The capillary tubes were then drawn off and sealed, as at *a* and *b*, by momentary contact with the flame of a spirit-lamp, and the closed ends were protected from injury during the journey by small caps of glass tube fitted with corks. The analyses of the air thus obtained were executed by means of hydrogen, in a eudiometer of Regnault's contrivance. The same apparatus was used by myself in the analyses of the air collected by Mr. Welsh. Frankland found 20·96 of oxygen in air collected by himself from the summit of Mont Blanc.

The following are results of some of the most trustworthy experiments upon the weight of air, calculating from the experiments

	Grains at 60° F. 30 in. Bar.	Grammes at 0° C. 760 mm.
of Dumas and Boussingault . . . . .	31·086	1·299500
of Biot and Arago . . . . .	31·074	1·299100
of Prout . . . . .	31·0117	1·296460
of Regnault . . . . .	30·935	1·293187

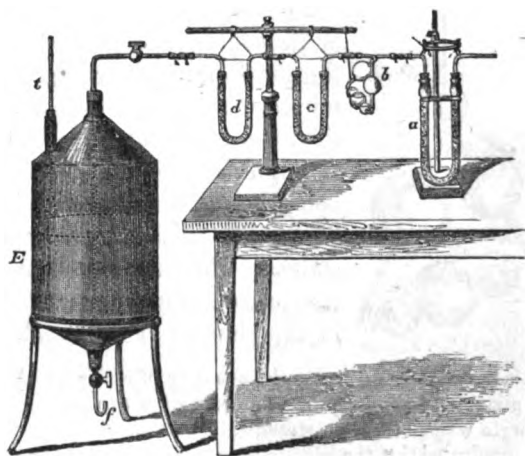
The second result is probably the most accurate, for it exactly corresponds with the density deduced from that of a mixture of oxygen and nitrogen in the proportions in which they occur in the atmosphere. A cubic metre of air, according to this result, at 0° C. and 760<sup>mm</sup> pressure, weighs 1·2991 kilogramme, or a cubic foot under a pressure of 30 inches Bar., weighs 536·96 grains at 60°. The weight of a given volume of air at 60° F., under a pressure of 30 inches Bar., is therefore only  $\frac{7}{8\frac{1}{2}}$  of that of an equal bulk of water at the same temperature, or  $\frac{7}{11\frac{1}{2}}$  at 0° C., and 760<sup>mm</sup> barometric pressure. Owing to the greater solubility of oxygen than of nitrogen, rain water and melted snow always contain a larger proportion of oxygen than the air itself, amounting to about 34 per cent. of the air dissolved, or nearly one volume of oxygen to two volumes of nitrogen. This is a

circumstance of great importance to aquatic animals, and one which could occur only in consequence of the air being a mechanical mixture and not a chemical compound of the two gases (64).

In addition to oxygen and nitrogen, the atmosphere contains a certain proportion of carbonic anhydride, a variable but minute trace of ammonia, traces of nitric acid, and of some compound of carbon and hydrogen, and frequently in towns a perceptible amount either of sulphurous anhydride or of sulphuretted hydrogen. Aqueous vapour is of course also present at all times, although its amount is liable to extensive fluctuations.

(341) *Estimation of Aqueous Vapour*.—The amount of aqueous vapour at any spot may be ascertained by means of the hygro-

FIG. 283.

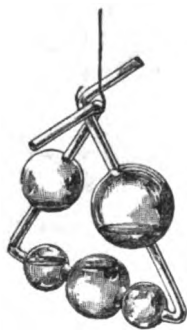


This vessel having been filled with water, is allowed to empty itself slowly by opening a stopcock, *f*, which terminates in a tube bent upwards to prevent the entrance of air at the bottom; a known volume of air is thus drawn through the tube *a*, which retains all the moisture. If the weight of this tube be determined before commencing the experiment, and a second time after it is completed, the increase in weight will indicate the amount of moisture in the bulk of air operated upon. The temperature is ascertained by means of the thermometer, *t*, and the atmospheric pressure is obtained by an observation of the barometer at the time. The flow of water from the aspirator is rendered uniform during the whole course of the experiment, by making the tube which conveys the air sufficiently long to reach nearly to the bottom of the vessel, as

shown by the dotted line which passes down from the central opening at the top.

(342) *Estimation of Carbonic Anhydride.*—The quantity of carbonic anhydride in the air may be determined in the course of the same experiment. If the bulbs at *b* be filled with a strong solution of caustic potash (sp. gr. 1.25), and the tube *c*, with fragments of fused potash, the gain in weight experienced by the tubes *b* and *c* will indicate the quantity of carbonic anhydride which has been absorbed in the operation; the bent tube, *d*, is filled with pumice-stone moistened with sulphuric acid; it is not weighed, but is merely interposed as a measure of precaution between the aspirator *e*, and the tube *c*, to prevent any accidental trace of moisture from passing backwards into *c*. The bulbs seen at *b* are to be filled with solution of caustic potash to the extent

FIG. 284.



shown in the enlarged drawing, fig. 284. This form of apparatus was contrived by Liebig. It is in continual requisition in the laboratory, for the purpose of absorbing gases which are transmitted through it; by placing it a little on one side, the gas is made to bubble up successively through each of the three lower bulbs, besides being brought thoroughly into contact with the liquid in the narrow portions of tubing which connect the different bulbs together. This simple contrivance has added greatly to precision in experiments of this kind.

Pettenkofer estimates the quantity of carbonic anhydride in air by agitating a given volume of the air for trial with a measured amount of lime-water or baryta water of known strength. The lime or baryta-water used for this purpose is graduated by the alkalimetric method, by means of a standard solution of oxalic acid. The carbonic anhydride neutralizes and precipitates a certain quantity of lime or baryta in the form of carbonate, and the quantity of lime or baryta which remains in the solution after the experiment is again determined by the solution of oxalic acid. The difference in the quantity of lime or baryta before and after its action upon the air enables the operator to calculate the proportion of carbonic anhydride with great accuracy.

The proportion of carbonic anhydride in the atmosphere varies from 3 to 6 parts in 10,000 of air. De Saussure found that within these limits its amount is lessened after rain, owing to the solvent action of the descending shower, which carries a portion of the gas with it to the earth. It increases during a frost, and diminishes when a thaw sets in. It is more abundant in summer than in winter. During the night it increases, and diminishes again after sunrise. It is less in amount over large

bodies of water than over large tracts of land. The proportion of carbonic anhydride is less liable to vary on elevated mountains, where it is generally more abundant than in the plains. It is also more abundant in densely populated districts than in the open country. In inhabited dwellings, and in rooms for public assemblies, the proportion of carbonic anhydride may, however, greatly exceed the normal amount.

The quantity of ammonia and nitric acid in the atmosphere is materially diminished after long-continued and heavy rains. Occasionally, from local and accidental circumstances, other gases and vapours are also met with. The air of towns contains in addition certain organic impurities in suspension. Angus Smith has attempted to estimate their amount by measuring the quantity of a very dilute solution of potassic permanganate of known strength which a given bulk of air will deprive of colour.—(*Q. J. Chem. Soc.* xi. 217, and *Report on Air in Mines*, 1864, p. 53.)

The average composition of the atmosphere in the climate of England may be approximately stated as follows, in 100 parts by volume :—

*Average Composition of the Atmosphere.*

Oxygen	...	...	...	...	20'61
Nitrogen	...	...	...	...	77'95
Carbonic anhydride	...	...	...	...	'04
Aqueous vapour	...	...	...	...	1'40
Nitric acid	...	...	...	...	} traces
Ammonia	...	...	...	...	
Carburetted hydrogen	...	...	...	...	
and in { Sulphuretted hydrogen	...	...	...	...	} traces
towns { Sulphurous anhydride	...	...	...	...	

If air which has been scrupulously freed from carbonic anhydride be passed over a column of pure ignited cupric oxide, traces of carbonic anhydride are always obtained, owing to the oxidation of some combustible compound of carbon. In the junctions of the apparatus employed for this experiment the use of cork and caoutchouc must be avoided (Karsten), or otherwise the carbonic anhydride might be derived from them.

## CHAPTER III.

### WATER. — HYDROGEN.

§ I. WATER :  $H_2O = 18$  ; *Atomic and Mol. Vol. of Vapour*    ;  
*Rel. wt.* 9 ; *Sp. Gr. as Vapour* 0'622, *as Liquid* 1'000, *as Ice* 0'918.

(343) ON the uses of water it is almost needless to enlarge, for they are universally felt and appreciated. In each of its

three physical conditions, the blessings which it confers upon man are inestimable. As ice, it furnishes in northern lands for months together, a solid bridge of communication between distant places : in the liquid condition, it is absolutely necessary to the existence of vegetable and animal life ; in this shape, too, it furnishes to man a continual source of power in the flow of streams and rivers ; it supplies one of the most convenient channels of communication between places widely separated ; and further, it is the storehouse of countless myriads of creatures fitted for use as food : in the state of vapour, as applied in the steam-engine, it has furnished a power which has in later years done more than any other physical agent to advance civilization, to economize time, and to ameliorate the social condition of man. In each and all of these points, if rightly considered, we must perceive the entire adaptation of this wonderful compound to the ends which it was designed by the Creator to fulfil.

Glancing at the physical condition of our planet, we cannot fail to be impressed with the important effects produced by the movements of water at periods anterior to the existence of man, as well as in more recent times. To such causes must we refer the formation of sedimentary rocks, and their arrangement in successive strata upon the surface of the earth : even now, observation shows that denudation is proceeding at some points, elevation and filling-up of hollows at others ; whilst the accumulation of drift and a variety of other extensive geological changes must be traced to the same ever-acting and widely operating agency.

It may further be observed that there is no form of matter which contributes so largely as water to the beauty and variety of the globe that we inhabit. In its solid state we are familiar with it in the form of blocks of ice, of sleet and hail, of hoarfrost fringing every shrub and blade of grass, or of snow protecting the tender plant, as with a fleecy mantle, from the piercing frosts of winter. The rare but splendid spectacles of mock suns, or parhelia, are due to the refractive power of floating spiculæ of ice upon the sun's rays. In its liquid condition, as rain or dew, it bathes the soil ; and the personal experience of all will testify to the charm which the waterfall, the rivulet, the stream, or the lake, adds to the beauty of the landscape ; whilst few can behold unmoved the unbounded expanse of ocean, which, whether motionless, or heaving with the gently undulating tide, or when lashed into foam by the storm that sweeps over its surface, seems to remind man of his own insignificance, and of the power of Him who alone can lift up or quell its roaring waves.

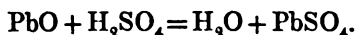
In vapour how much variety is added to the view by the mist or the cloud, which by their ever-changing shadows diversify, at every movement, the landscape over which they are flitting; whilst the gorgeous hues of the clouds around the setting sun, and the glowing tints of the rainbow, are due to the refractive action of water and watery vapour upon the solar rays.

*Properties.*—At the ordinary temperature of the air, water, when free from admixture, is a clear, colourless, transparent liquid, destitute of taste or smell. At temperatures below  $32^{\circ}$  ( $0^{\circ}$  C.) it freezes and assumes a variety of crystalline forms derived from the rhombohedron and six-sided prism. Water evaporates at all temperatures, and under the ordinary pressure of the atmosphere it boils at about  $212^{\circ}$  ( $100^{\circ}$  C.). Its anomalous expansion by heat (143), and the important purposes thereby attained (151), as well as the great dilatation which it undergoes on freezing (76), have been already pointed out. Arago and Fresnel have shown, that notwithstanding the gradual dilatation of water at temperatures below  $39^{\circ}2$  ( $4^{\circ}$  C.), its refractive power on light continues to increase regularly, as though it contracted. Its density at  $4^{\circ}$  is taken as 1.000, and it forms the standard with which the specific gravities of all solids and liquids are compared. A litre of water, or cube of 10 centimetres in the side, at  $4^{\circ}$  C. weighs 1000 grammes, or 1 kilogramme; or in English weights and measures, a cubic inch of water at  $62^{\circ}$  F. weighs in air 252.456 grains, and a cubic foot very nearly 1000 (more exactly 997) ounces avoirdupois.

To the chemist water is invaluable as a solvent. It is the perfection of a neutral substance; and it enters into combination most extensively both with acids and with bases. Experience has shown that when an anhydride, or so-called anhydrous acid, has once been allowed to combine with water, the entire separation of the water from the compound is often impracticable, unless some powerful base be presented to the acid; in such a case the base appears to displace the water, and its expulsion by heat is then easily effected. Suppose, for example, that sulphuric acid has been freely diluted with water; upon the application of heat the water at first passes off readily, leaving the less volatile acid behind. By degrees, however, it becomes necessary to increase the temperature in order to expel the water, and at last the acid begins to evaporate also, and finally no further separation can be effected, because when the temperature rises to about  $640^{\circ}$  ( $338^{\circ}$  C.) the entire liquid distils over. It is found on analysing the acid when it has reached this point, that the composition of



the liquid may be represented by the formula  $\text{H}_2\text{SO}_4$ . But if to this concentrated acid, a base, such as oxide of lead, be added, the water is easily expelled, and anhydrous plumbic sulphate is obtained :—



Upon the older view of the constitution of salts, which regards these bodies as formed by the union of an anhydride with a base, the water would in the foregoing instances supply the place of a base, and it hence has been termed *basic water*, e.g. :—(if  $H = 1$ ,  $O = 8$ ,  $S = 16$  and  $Pb = 103$ ) :

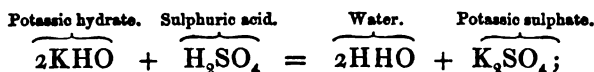
$\text{HO}, \text{SO}_4$ , oil of vitriol:  $\text{PbO}, \text{SO}_4$ , sulphate of lead.

Still adopting the older view, it has been supposed in a similar manner that water combines with the powerful bases, such as potash or soda; it then cannot be expelled from them until some acid has been added. Potash in the form in which it is obtained by evaporating down its aqueous solution and heating the residue to dull redness, contains the elements of one equivalent of the alkali and one of water ( $\text{KO}, \text{HO}$ ): this equivalent of water cannot be expelled except by the addition of an acid, such as sulphuric acid; then, by the application of heat, anhydrous potassic sulphate is obtained ( $\text{KO}, \text{HO} + \text{HO}, \text{SO}_4 = 2\text{HO} + \text{KO}, \text{SO}_4$ .) In such a case the water in combination with the base appears to perform the part of an *acid*.

This older explanation is inadmissible if water be represented as consisting of  $\text{H}_2\text{O}$ ; yet in the latter case the presence of hydrogen in potassic hydrate may be equally well accounted for, if it be supposed that caustic potash is a compound formed upon the same plan or type as water, but that it contains an atom of potassium in place of one of the atoms of hydrogen present in the molecule of water. Further, anhydrous potash (which may be formed from the hydrate of the alkali by heating it with potassium, whilst hydrogen is liberated) is viewed as containing two atoms of potassium in place of the two atoms of hydrogen in the molecule of water. These relations of the three different compounds may be thus represented :—



The reaction of sulphuric acid upon potassic hydrate is then a true case of double decomposition, as may be thus represented :—



the two atoms of potassium of the base, and the two of hydrogen in the acid, changing places with each other, whilst potassic sulphate and water are each formed simultaneously.

The compounds of water are frequently termed *hydrates*.

When a body is described as being entirely free from water, in combination, it is commonly said to be *anhydrous* (from *ἀ* not, *ὕδωρ* water).

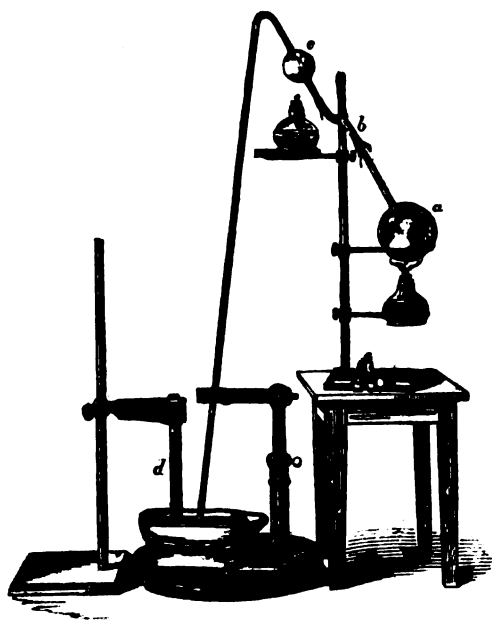
Many salts in crystallizing unite with a definite quantity of water, which is essential to the form of the salt, but which may, by the application of a gentle heat, be expelled without altering the chemical properties of the saline body. In this case the water is spoken of as *water of crystallization*. Many salts part with such water by mere exposure to air. Sodid carbonate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) for example, crumbles down or *effloresces* to a white powder; and the same thing occurs in the case of sodid sulphate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ). Other salts, on the contrary, absorb moisture from the atmosphere, and become damp or even liquefy in the water so absorbed; they are then said to *deliquesce*. Potassic carbonate ( $\text{K}_2\text{CO}_3$ ) and calcic chloride offer instances of this kind. The form of the salt depends upon the quantity of this water of crystallization. For instance, borax is always found to crystallize with 10 atoms of water ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), in oblique rectangular prisms, if the solution of the salt be not sufficiently concentrated to begin to crystallize till the temperature falls to  $133^\circ$  ( $56^\circ \text{C.}$ ); but from a more concentrated solution borax is deposited in regular octohedra with only 5 atoms of water. So, again, sodid sulphate crystallizes, under ordinary circumstances, in oblique four-sided prisms with 10 atoms of water; but if a solution saturated at  $91^\circ$  ( $33^\circ \text{C.}$ ), be very slowly raised to the boiling point, the sulphate is deposited in rhombic octohedra which contain no water.

(344) *Various kinds of Natural Waters*.—Owing to its extensive solvent powers, water is never met with naturally in a state of purity. *Rain water*, collected after a long continuance of wet weather, approaches nearest to it, but even that always contains atmospheric air, and the gases floating in the air, to the extent of about  $2\frac{1}{2}$  volumes of air in 100 of water. The first fall of rain after an interval of dry weather always contains traces of nitrates and of salts of ammonium, and often of common salt and some organic impurities.

The quantity of air which is contained in spring or other water can be readily ascertained in the following manner. A globular flask, *a*, fig. 285, capable of containing 400 or 450 cub. centim., or from 14 to 16 ounces, such as is used for taking the density of vapours, is filled with the water to be examined, and connected by a vulcanized caoutchouc tube, *b*, to a piece of barometer tube, upon which is blown a bulb, *c*, 2 inches (5 cm.) or more in diameter. This tube is bent in the manner represented in the figure; the longer limb being upwards of 30 inches (760<sup>mm.</sup>) in length, and terminating below in a recurved extremity

designed to deliver the gas disengaged from the water, into a graduated jar, *d*, with an expanded funnel-shaped mouth, which is supported in a small mercurial

FIG. 285.



bath. The bulb, *c*, having been about half filled with the water, is connected with the flask by the caoutchouc tube, which is firmly secured at both ends by ligatures. A small wooden vice, such as is seen at *f*, is made use of to compress the vulcanized tube and to cut off communication between the flask and the bulb, *c*. The water in *c* is now made to boil briskly for ten minutes or a quarter of an hour, until all the air is expelled from the tube, the mouth of which is kept just below the surface of the mercury. When, after the boiling has been continued for a few minutes, no more air escapes from the tube, the jar, *d*, is filled with mercury and placed over the end of the long tube. The vice is removed, and heat applied to the flask; the water speedily begins to give

off gas; and the quantity increases till the water boils. The ebullition must be continued steadily for a full hour, and the operation terminated by a few minutes' brisk boiling, by which the delivery tube will be filled with steam, and all the air will be driven over into the jar. One object of the globe, *c*, is to prevent the water from boiling over into the jar, *d*: a little steam always condenses in the jar above the mercury, but this is a matter of small consequence. When the operation has terminated, the gas is allowed to cool, and is transferred to a tall jar of water, or of mercury, where its bulk can be measured.

It will be found that all water, including even that which has been recently distilled, contains air. For example, three samples of water twice distilled in glass vessels, were submitted to experiment: 100 cub. centim. of the first specimen contained 1.85 c. c. of air; in the same bulk of the second 2.15, and the third specimen 2.38 c. c. of air were present; the oxygen and nitrogen being in each case almost exactly in the proportion of 1 measure of oxygen to 2 measures of nitrogen.

*Spring Water*, although it may be perfectly transparent, always contains more or less of saline matter dissolved in it; the nature of these salts will of course vary with the character of the soil through which the water percolates. The most usual saline impurities are calcic carbonate and sulphate, common salt, and magnesian sulphate and carbonate. The waters of the New Red Sandstone are impregnated to a greater or less extent with calcic

sulphate; and the shallow wells in the gravel of the London district contain a considerable quantity of the same salt, to which they owe their hardness. Nitrates are often abundant in these and other well-waters of towns, owing to contamination with sewerage products, which have in many cases undergone partial oxidation. The nature and amount of the salts found in the waters of shallow wells vary considerably at different times, but the deep springs are very uniform when examined even at considerable intervals. Most spring waters are charged with a notable proportion of carbonic acid, which dissolves a considerable amount of calcic carbonate; the calcareous springs in the chalk districts around London contain from 250 to 285 mgrms. per litre, or from 18 to 20 grains of chalk per gallon, nearly one-third of which becomes separated by exposure of the water to the atmosphere, so that a running stream will seldom contain more than 12 or 14 grains of chalk per gallon in solution (180 or 200 mgrms. per litre). Waters which have filtered through a bed of chalk also often contain sodic carbonate in considerable quantity, as is the case with the deep-well waters of London.

*Mineral Waters* are waters impregnated with a large proportion of any one of the above-named salts, or with some substance not so commonly met with: such waters are usually reputed to possess medicinal qualities, which vary with the nature of the salt in solution. Many of these springs are of a temperature considerably higher than that of the surface of the earth where they make their appearance. At Carlsbad and Aix-la-Chapelle this temperature varies from 160° to 190° (71° to 88° C.). Such hot springs either occur in the vicinity of volcanoes, in which case they generally abound in carbonic acid, as well as in common salt and other salts of sodium: or they spring from great depths in the rocks of the earliest geological periods, and contain chlorides of calcium and magnesium, and almost always traces of sulphuretted hydrogen. (Berzelius.) The Geysers of Iceland are heated even beyond the temperature of 100° C. in the tube, and at intervals the boiling water is ejected with explosive violence. (See Tyndall, *Heat as a Mode of Motion*, 1st ed. 119.)

Many mineral waters contain salts of iron in solution, which impart to them an inky taste; they are then frequently termed *chalybeate* waters; the Tunbridge Wells springs, and some of those at Cheltenham are of this kind. In other instances carbonic acid is very abundant, giving the brisk *effervescent* character noticed in Seltzer water, which also contains a notable propor-

tion of sodio-hydric carbonate ( $\text{NaHCO}_3$ , the so-called bicarbonate of soda), and the Vichy waters abound still more in this salt. Less frequently, as in some of the Harrogate and Moffat waters, sulphuretted hydrogen is the predominating ingredient, giving the nauseous taste and smell to such *sulphureous* waters. In other instances, the springs are merely *saline*, and contain purgative salts, like the springs at Epsom, which abound in magnesian sulphate, and at Cheltenham, where common salt and sodic sulphate are the predominant constituents. Many of these saline springs also contain small quantities of iodides and bromides, which add greatly to their therapeutic activity. The Geysers are rich in silica, which in some cases forms nearly one-half of their soluble constituents.

*River Water* is less fitted for drinking than ordinary spring water, although it often contains a smaller amount of salts; for it usually holds in solution a much larger proportion of organic matter of vegetable origin, derived from the extensive surface of country which has been drained by the stream. If the sewerage of large towns situated on the banks be allowed to pass into the stream, it is of course still less fit for domestic use. Running water is, however, endowed with a self-purifying power of the highest importance; the continual exposure of fresh surfaces to the action of the atmosphere promotes the oxidation of the organic matter, and if the stream be unpolluted by the influx of the sewerage of a large town, this process is generally fully adequate to preserve it in a wholesome state. River water almost always requires filtration through sand before it is fit for domestic use; and if water-works designed to supply such water be properly constructed, provision is made for this filtration. Suspended matters, such as weeds, fish-spawn, leaves, and finely divided silt or mud, are thus removed; but vegetable colouring matter in solution, salts, and other bodies, when once they are dissolved, cannot be arrested by such a filter.

In the gradual percolation of water through the porous strata of the earth, many even of these soluble impurities are removed, particularly those of organic origin, partly by adhesion to the surface of the filtering material, but chiefly by a slow oxidation in the pores of the soil.

The magnetic oxide of iron, indeed, seems to exert a peculiar influence in promoting the oxidation of organic matter contained in water which is allowed to percolate through it, and it appears to be probable that this action, to which Mr. Spencer has particularly called attention, may furnish a valuable auxiliary to the

methods of filtration at present in use. Filtration through beds of iron turnings has likewise been practised in some cases with advantages of a similar description, but the oxygen is in this case in great measure absorbed from the water by the iron. Animal charcoal also exerts as remarkable effect in promoting the oxidation of organic matters in solution, and it constitutes an excellent filtering material.

The presence of organic matter in water is easily ascertained by the reducing influence which it exerts upon chloride of silver or of gold, when boiled with them. The argentic chloride becomes purplish; and auric chloride imparts a brown tint to the water under such circumstances, owing to the precipitation of metallic gold. Even at ordinary temperatures a very dilute acidulated solution of potassic permanganate is rendered nearly colourless, by reduction to a lower state of oxidation.

Water is familiarly spoken of as *hard* or *soft*, according to its action on soap. Those waters which contain compounds of calcium or magnesium occasion a *curdling* of the soap, as these bodies produce with the fatty acid contained in the soap a substance not soluble in water. Soft waters do not contain these salts, and dissolve the soap without difficulty. Many hard waters become softer by boiling; in such cases the carbonic acid is expelled, and the calcic carbonate and part of the calcic sulphate which were held in solution are deposited, and cause a 'fur' or incrustation upon the inside of the boiler. Such waters admit of being softened considerably by the addition of a certain proportion of lime water (655). When the hardness is owing to calcic or magnesian sulphates, the addition of sodic carbonate precipitates the carbonates of these metals and softens the water, as is practically known to laundresses.

*Sea Water* is largely impregnated with common salt, and with magnesian chloride, to which it owes its saline bitter taste. It might be supposed that the quantity of salts which it contains is continually on the increase, as the sea is the receptacle for all the fixed contents of the river water which is discharged into the ocean, since pure water alone evaporates from its surface; but here also there is a return to the surface of the soil provided for in the marine plants, the fish, and their representative guano, which are perpetually being raised from its depths by the force of storms, by predatory birds, and by the industry of man. The specific gravity of sea water is subject to trifling variations, according to the part of the globe from which it is taken. The waters of the Baltic and of the Black Sea are less salt than the

average, while those of the Mediterranean are more so. The waters of the Mediterranean in the Levant are more salt than those of the same sea near the Straits of Gibraltar. The mean specific gravity of sea water is 1.027, and the quantity of salts ranges from 3.5 to 4 per cent. According to Schweitzer (*Phil. Mag.* 1839, xv. 58), the water of the British Channel is composed as follows:—that of the Mediterranean, analysed by Usiglio (*Ann. de Chimie*, III. xxvii. 104), will be seen to agree very closely with it in composition:—

			British Channel.		Mediterranean.
Water	...	...	963.74372	...	962.345
Sodic chloride	...	...	28.05948	...	29.424
Potassic chloride	...	...	0.76552	...	0.505
Magnesian chloride	...	...	3.66658	...	3.219
Magnesian bromide	...	...	0.02929	...	0.556
Magnesian sulphate	...	...	2.29578	...	2.477
Calcic sulphate	...	...	1.40662	...	1.357
Calcic carbonate	...	...	0.03301	...	0.114
Iodine	...	...	traces		
Ammonia	...	...	traces		
Ferric oxide	...	...		...	.003
			<hr/>		<hr/>
			1000.00000		1000.000
			<hr/>		<hr/>
Specific gravity	...	...	1027.4 at 16° C.		1025.8 at 21° C.

An elaborate paper on the composition of sea water in various parts of the world, by G. Forchhammer, will be found in the *Phil. Trans.* for 1865. Minute quantities of manganese, barium, strontium, and aluminum, as well as of silica, boracic acid, and phosphates, have been found in the waters of the ocean, but nitrates have as yet eluded the most careful observation.

(344a) For chemical purposes water is always purified by distillation, which may be effected on a small scale in glass retorts, but it is generally carried on in a copper still provided with a pewter or copper worm. Iron pipes may also be safely used for the purpose of condensation; but lead must be avoided. The still should not be employed for any other purpose. The addition of lime to the water before submitting it to distillation is useful, as it retains the excess of carbonic acid, and also traces of hydrochloric acid, which if magnesian chloride be present are apt to come over, owing to the decomposition of this salt. The first portions of water should be rejected, because they usually contain traces of ammonia: when a few drops of distilled water are evaporated upon a slip of glass, no stain or mark should be left, otherwise some saline impurity is present.

Distilled water is now largely prepared on long sea voyages, the ships of H.M. Navy being fitted with suitable distillatory apparatus. Organic matter is present both in ordinary water and in sea water; a part of this undergoes decomposition during distillation, and gives a mawkish odour to the distillate. This, however, is entirely got rid of by filtration through charcoal, after due aëration, and the filtered water is then agreeable and wholesome as a beverage.

Water was long supposed to be an elementary substance. This, however, is not the case: it is a compound of oxygen with hydrogen, in the proportion of two atoms of hydrogen to one atom of oxygen; its symbol is therefore  $H_2O$ , and its combining number 18. When converted into vapour, 18 grammes of steam occupy twice the bulk of 1 gramme of hydrogen at the same temperature; the atomic and molecular volume of aqueous vapour is therefore  $\square$ , if the atomic volume of hydrogen be taken as  $\square$ . Its composition is shown in the following table:—

	Symb.	By weight.	Dumas.	By vol.	Sp. gr. vap.
Hydrogen	$H_2$	= 2 or 11.11	11.12	2 or 1.0	= 0.0692
Oxygen	O	= 16 88.89	88.88	1 0.5	= 0.5528
Water	$H_2O$	= 18 100.00	100.00	2 1.0	= 0.6220

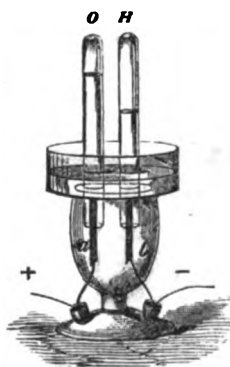
## § II. HYDROGEN: $H=1$ .

*Sp. Gr.* 0.0692; *Atomic Vol.*  $\square$ \*; *Rel. wt.* 1; *Monad.*

(345) *Preparation.*—The composition of water may be determined both by analysis or separation of its constituents, and by synthesis or their re-union after such separation.

1.—An elegant mode of showing the composition of water analytically is afforded by the voltaic battery. A glass vessel, fig. 286, containing two platinum plates, *a* and *b*, is filled with water, slightly acidulated with sulphuric acid to improve its conducting power, and is arranged so as to transmit the current of a battery consisting of three or four pairs of Grove's cells (266). Immediately that the two platinum plates are connected with the wires of the battery, gas rises from each; and if two similar jars be filled with water and

FIG. 286.



\* Free hydrogen is now regarded as  $(HH)$ , or *hydride of hydrogen*, with a molecular volume  $\square$ , and *molecular weight* = 2.

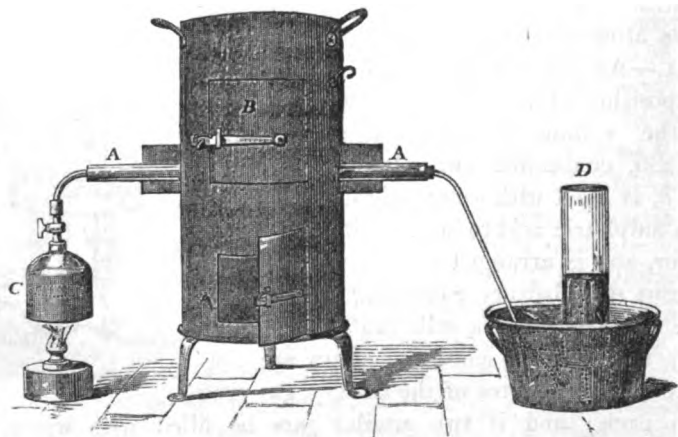


inverted one over each plate, the volume of the gas which rises from the platinode, or negative plate, *b*, will be found to be exactly double of that which rises from the zincode, or positive plate, *a*: the gas in the tube *o* will show itself to be oxygen by rekindling a glowing match, whilst that in *h* extinguishes flame, but takes fire itself when a light approaches it. To the latter gas the name of *hydrogen* (from ὕδωρ water, γεννάω to generate) has been given. Oxygen and hydrogen are the sole ingredients of water, and by their union in the proportion of two measures of hydrogen to one measure of oxygen this liquid is reproduced.

2.—The presence of hydrogen and oxygen in water may be shown in other ways, and hydrogen may be obtained from it by chemical means. If a piece of sodium of the size of a pea be wrapped up in blotting paper, and be rapidly introduced beneath the mouth of a strong wide tube, 10 or 12 inches (25 or 30 cm.) long, filled with water and inverted in the pneumatic trough, bubbles of gas will be quickly disengaged, and will collect in the upper part of the tube. On inverting the tube and applying a light, the gas will take fire and burn with flame; the liquid in the tube will be found to be alkaline, and will change the yellow colour of turmeric to brown: sodic hydrate having been formed by the displacement of half of the hydrogen in the molecule of water by the equivalent of sodium;  
 $2\text{H}_2\text{O} + \text{Na}_2 = 2\text{NaHO} + \text{H}_2.$

3.—Hydrogen may be also obtained by the action of water

FIG. 287.

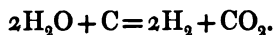


upon iron at a high temperature. In order to effect this, let a piece of iron piping, shown at *A A*, fig. 287, be filled with iron

turnings, and heated to redness in a portable furnace, B; and let a current of steam be driven through the tube from a small boiler, C, attached to one extremity of the pipe; the aqueous vapour in its passage will be decomposed, the oxygen will enter into combination with the heated iron, magnetic oxide of iron being formed, whilst the liberated hydrogen will pass on, and may be collected over water in a jar, D, placed over the mouth of a bent tube attached to the other extremity of the iron pipe. The decomposition may be represented in symbols as follows:—

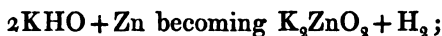


4.—Deville and Debray prepare hydrogen on a large scale nearly pure, by transmitting steam over charcoal, or coke, heated to dull redness. Carbonic anhydride and hydrogen are the sole products if the temperature be kept sufficiently low:—



The gas is purified by causing it to traverse an apparatus filled with slaked lime, and similar to that known as the dry lime purifier for coal gas. If the temperature be allowed to rise too high, part of the carbonic anhydride is converted into carbonic oxide (357), and this gas cannot then be removed from the mixture.

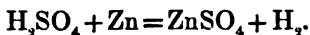
5.—Hydrogen may also be obtained by heating zinc with a solution of potassic hydrate, the metal displacing the hydrogen contained in the hydrate, whilst the compound of zinc as it is formed, is dissolved by the alkaline liquid—



but this method is interesting from its theoretical bearings rather than from any practical utility.

6.—But the most convenient way of procuring hydrogen is by the action of diluted sulphuric acid on zinc. The zinc may be melted in an iron ladle, and poured from the height of a metre into a pail of cold water, by which means it is *granulated*, or reduced into grains or flakes: about half an ounce (15 grms.) of the granulated zinc is introduced into a retort, and about 7 ounces (200 c. c.) of a diluted acid, prepared by mixing one part of oil of vitriol cautiously with 6 parts of cold water, stirring all the while, is poured upon the zinc. Hydrogen gas is soon evolved in great abundance: the first portions of gas which are contaminated with the air contained in the retort, must be allowed to escape; afterwards the gas may be collected in the usual way. In this process the zinc may be regarded as displacing the hydrogen of the acid, and forming the salt called sulphate of zinc, or zincic sulphate,

which becomes dissolved, while the hydrogen passes off in the gaseous form. The change may be illustrated by the following equation:—



An ounce of zinc is sufficient to liberate from water about  $2\frac{1}{2}$  gallons of the gas, or 30 grms. will furnish about 10 litres. Scraps of iron may be substituted for zinc; but in this case the gas is less pure: it has a disagreeable odour, due to the presence of a peculiar compound of hydrogen and carbon, but this may be removed by allowing the gas to stream through a tube filled with fragments of wood-charcoal (Stenhouse). The gas furnished by the action of diluted sulphuric acid on zinc also possesses a peculiar odour, and is frequently contaminated with small quantities of compounds of hydrogen with sulphur, arsenicum, and carbon. It may be freed from these impurities by causing it to pass first through a strong solution of potash, and then through a solution of corrosive sublimate, or of nitrate of silver.

*Properties.*—Hydrogen is an elementary substance, which was discovered by Cavendish in 1766, and was called by him *inflammable air*. When obtained with the precautions just mentioned, it is a colourless, transparent, tasteless, and inodorous gas. Its refractive power upon light is higher than that of any other gas, being more than six times as great as that of atmospheric air at the same temperature, when the hydrogen is compressed till its weight is the same as that of an equal bulk of air. It has never been liquefied, and is even less soluble in water than nitrogen, 100 volumes of water, according to Bunsen, dissolving 1.93 vols. of hydrogen at all temperatures between  $32^\circ$  and  $68^\circ$  ( $0^\circ$  and  $20^\circ$  C.). Hydrogen is the lightest form of matter which is known: its weight is only one-sixteenth of that of an equal bulk of oxygen, and a little less than a fourteenth of that of air; 1 litre at  $0^\circ$  C. and 760<sup>mm</sup>. Bar. weighs 0.0896 grm., or 100 cubic inches of it at  $60^\circ$  F. and 30 in. Bar., weigh but 2.14 grains. Owing to its levity, it has been extensively used for aërostatic purposes, although the facility with which coal-gas can now be obtained, has caused this latter, notwithstanding its much greater density, to be universally substituted for hydrogen in filling balloons.

A light bag made of the craw of a turkey, or of collodion, may easily be inflated with hydrogen, and will ascend rapidly, and carry with it a weight of several grains. Owing to the lightness of the gas, a jar may be easily filled with it by *displacement* without using the pneumatic trough:—A tube, 8 or 10 inches (20 or 25 centimetres) long, is fixed by a cork, in the manner shown at

A, fig. 288, into a three-necked bottle containing some granulated zinc; diluted sulphuric acid is introduced through the funnel, and the gas, after the atmospheric air in the bottle has been allowed to escape, may be collected by holding a jar over the tube, as at B. The hydrogen will be retained for some minutes even if the jar be removed, provided that it be still held in the inverted position; while if the mouth be turned upwards, the gas will have escaped after the lapse of a few seconds.

FIG. 288.



Pure hydrogen, though it cannot support life, is not poisonous, and when mixed with a certain proportion of oxygen it has been breathed for some time without inconvenience; but owing to its rarity, it renders the voice temporarily much sharper and more shrill than usual.

Hydrogen unites directly with several elements if heated with them, particularly with oxygen and with chlorine. If heated with sulphur, with bromine, and with phosphorus, it also combines with them, though slowly and with difficulty.

Hydrogen has a smaller combining number than any other elementary body, and it has hence been taken as the unit or standard of comparison, both for atomic weights and combining volume. Its proportional number is therefore unity, or 1, and its combining volume 1 or  $\square$ .

The proportion in which the different elements combine with hydrogen to form gaseous compounds affords a well-marked character which serves as a foundation for grouping the different elements into natural families. For example, in the table which follows, some of the most important gaseous compounds of the different elements with hydrogen are enumerated: in each case the quantity represented by the formula given indicates 2 volumes of the gaseous compound ( $H = 1$  vol.  $\square$ , and  $HH = 2$  vols.  $\square$ ).

Compounds of Monads.	Compounds of Dyads.	Compounds of Triads.	Compounds of Tetrads.
Hydrochloric Acid. $HCl$	Water. $H_2O$	Ammonia. $H_3N$	Marsh Gas. $H_4C$
Hydrobromic Acid. $HBr$	Sulphuretted Hydrogen. $H_2S$	Phosphuretted Hydrogen. $H_3P$	Siliciuretted Hydrogen. $H_4Si?$
Hydriodic Acid. $HI$	Seleniuretted Hydrogen. $H_2Se$	Arseniuretted Hydrogen. $H_3As$	
Hydrofluoric Acid. $HF$	Telluretted Hydrogen. $H_2Te$	Antimoniuretted Hydrogen. $H_3Sb$	

In the first column the compounds are formed by the union of one atom of

K 2

each compound. The metallic basyls of the alkalis and one or two other metals displace hydrogen from its compound with chlorine, in the proportion of single atoms, and these metals, with the halogens themselves, constitute the group of *Monads*.

In the second column of the table two atoms of hydrogen are shown in combination with one atom of certain other (*dyad*) elements. In addition to the non-metallic elements which thus have the power of supplying the place of two atoms of chlorine in combining with hydrogen, it may be stated that the metals of the alkaline earths and the ordinary metals which form basic oxides, displace two atoms of hydrogen, and unite with two atoms of chlorine; they constitute the dyad group of metals.

In the third column of the table each compound given contains 3 atoms of hydrogen united with 1 atom of some other (*triad*) element. These also have their representatives among the well-known metals; for the triads embrace gold, aluminum, and rhodium, an atom of each of which unites with three atoms of chlorine, and is thus equivalent in function to three atoms of hydrogen.

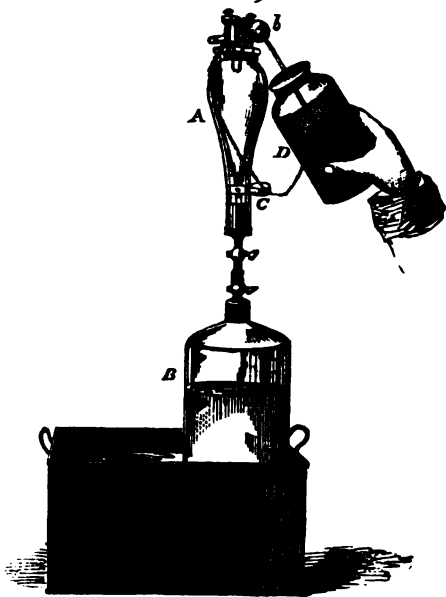
In the fourth column the compounds enumerated contain four atoms of hydrogen in combination with another (*tetrad*) element. Among the metals, platinum, tin, and a few other rarer elements discharge the functions of four atoms of hydrogen, each atom of the metal forming a stable compound with 4 atoms of chlorine.

(346) *Synthesis of Water—Eudiometers*.—Hydrogen is extremely inflammable; when a lighted taper is plunged into a jar of it, the gas takes fire, but the taper is extinguished. A jet of hydrogen burns with a pale, yellowish, feebly luminous flame, but gives out great heat. If the gas be dried by causing it to pass through a tube containing calcic chloride, and a cold bell-jar be held over the burning jet, the interior of the glass quickly becomes bedewed with moisture, owing to the formation of water by the union of the burning hydrogen with the oxygen of the atmosphere. Oxygen and hydrogen may be kept in a state of mixture at the ordinary temperature of the air for an unlimited period without entering into combination; but the passage of an electric spark, the application of a lighted or even of a glowing match, and, in some instances, the mere contact of a cold metallic substance, such as platinum, especially if the metal be in a finely divided state (65), is sufficient to determine their immediate combination. Sudden compression of the gases, when mixed, produces the same effect from the heat evolved, whilst a still greater amount of compression if it be gradually applied, even when raised till it is equal to that of 150 atmospheres, fails to produce their union.

Cavendish, in his inquiries respecting the formation of water, effected the combination of the two gases by means of the electric spark. He employed for this purpose a strong glass vessel, a modification of which is represented at A, fig. 289. Through the upper part two platinum wires are inserted to within  $3^{\text{mm}}$ , or the eighth of an inch of each other. The vessel can be closed at the bottom by a glass stopcock, C. The air is exhausted, and the vessel screwed upon the top of a jar, B, containing a mixture of two measures of hydrogen and one measure

of oxygen: on opening the stopcocks a portion of the mixture enters the vessel; the cocks are then closed; and an electric spark passed through the mixture, by discharging a small Leyden jar, *d*, through the platinum wires, *a*, *b*.\* A bright flash is seen at the moment of the discharge, and the gases combine, forming steam, which becomes condensed on the sides of the glass: the whole of the two gases, if mixed in the above proportions, enter into combination with each other. On again opening the stopcocks a fresh quantity of the gases may be admitted, to supply the place of those just condensed, the spark may be again transmitted, and the process may be repeated till the whole of the gases are consumed, and a considerable quantity of water formed.

FIG. 289.



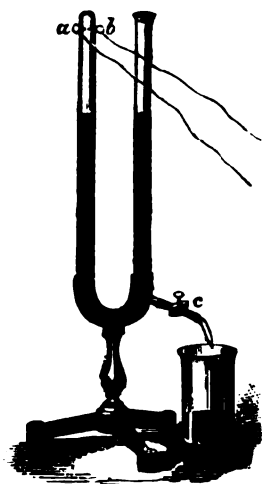
The uniformity of composition, and regularity of proportion in which compounds are produced when they combine chemically, is strikingly illustrated by means of a mixture of oxygen and hydrogen gases. The two gases may be mixed in any arbitrary proportion in a suitable vessel, into the sides of which two platinum wires are fused for the purpose of transmitting the electric spark. If the mixture be capable of exploding at all, the combination will be found to have occurred in the proportion of two measures of hydrogen to one measure of oxygen, no matter in what proportion the gases were mingled. If oxygen be used in excess, the superfluous oxygen will be found remaining uncombined; and if hydrogen be in excess, the excess of hydrogen will be left unaltered after the transmission of the spark.

Upon this principle a valuable instrument, the *Eudiometer*, is constructed, by means of which various gaseous mixtures may be analysed with great exactness. Many different forms of this instrument are in use. One of the most convenient is Hofmann's. It consists of a stout siphon tube, fig. 290, open at one extremity and closed at the other. Into the sides of the tube, near the sealed end, two platinum wires, *a*, *b*, are fused, for the purpose of transmitting an electric spark through the cavity of the tube. The sealed limb is accurately

\* The discharge from the secondary current of a Ruhmkorff's coil may in all such cases be advantageously substituted for the spark of the Leyden jar.

graduated to tenths of a cubic centimetre, or other suitable divisions. Suppose it be desired to ascertain the proportion of oxygen in atmospheric air; the instrument is first filled with mercury, after which a

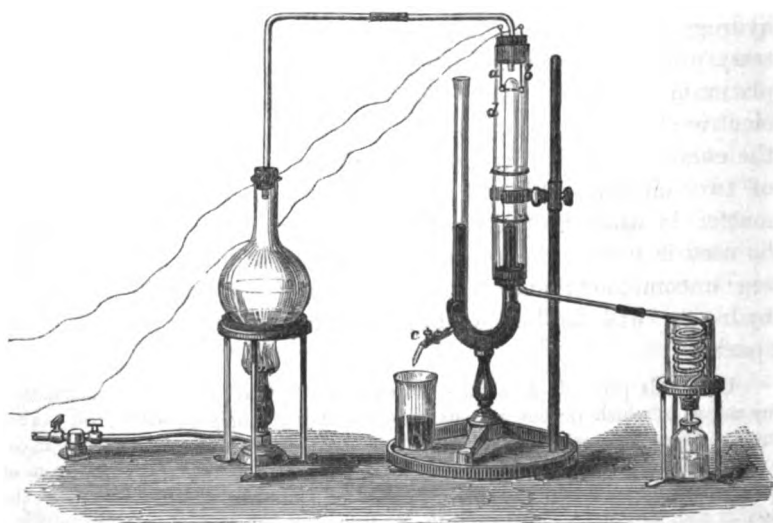
FIG. 290.



small quantity of air is introduced: the bulk of this air is accurately measured, taking care that the liquid metal stands at the same level in both tubes, which is easily effected by adding mercury, or by drawing off the mercury, if needed, through the caoutchouc tube which is fixed upon the small outlet tube just above the bend, and which is closed by means of a screw-tap, *c*. A quantity of pure hydrogen about equal in bulk to the air is next introduced, and the bulk of the mixture is again accurately measured. The open extremity of the tube is now closed with a cork, below which a column of atmospheric air is safely included; this portion of air acts as a spring which gradually checks the explosive force, when the combination is effected by passing a spark across the tube by means of the platinum wires. The mixture is then exploded by the electric spark. The remaining gas now occupies a smaller volume, owing to the condensation of the steam which has been formed. Mercury is therefore again poured into the open limb, until it stands at the same level in both

tubes, and the volume of the gas is measured a third time. One-third of the reduction in bulk experienced by the gas will represent the entire volume of

FIG. 291.



oxygen which the mixture contained. For accurate experiments, a very complete though expensive form of eudiometer upon this principle has been contrived by Regnault. (*Ann. de Chimie*, III. xxvi. 333.)

A modification of the foregoing experiment enables us to show that the

volume of aqueous vapour which is formed by the union of oxygen with hydrogen, occupies a space exactly equal to two-thirds of that of its constituent gases, or that 2 volumes of hydrogen and 1 volume of oxygen furnish by their union 2 volumes of steam.

For this purpose the closed limb of the siphon eudiometer is surrounded by a second wider tube, as shown at *d*, fig. 291, provided with an exit tube and condenser below. A mixture of two volumes of hydrogen and 1 of oxygen—such as is furnished by the electrolytic decomposition of water—is introduced into the sealed limb, of which it should occupy 5 or 6 inches (12 or 15<sup>cm.</sup>). A gentle current of vapour from a small flask, containing fousel oil, which boils at 259° (132° C.), is then maintained for some minutes through the wide tube, so as to bring the mixed gases to the temperature of 132° C. The mercury in the two limbs is levelled, and the height at which the expanded gas stands is then marked by means of an elastic band which slides on the outer tube. The eudiometer is next closed with a cork, and the electric spark transmitted, whilst the current of vapour is still maintained; the gases combine with a flash, and the volume of the vapour produced is seen to be less than that of its constituent gases. If now the mercury in the two limbs of the eudiometer is again levelled, it is seen that the aqueous vapour occupies a volume exactly two-thirds of that of the gases originally employed.

If a mixture of oxygen and hydrogen be fired in the air in considerable quantity, as when a bladder-full is ignited,—or, what is still better, when a quantity of soapsuds is blown up into a lather by forcing some of the gaseous mixture out of a bladder through a pipe under the liquid,—a loud and sharp report attends the combination; the steam which is formed expands suddenly from the high temperature attendant on the combustion, and immediately afterwards becomes condensed: great dilatation is first produced, followed by the formation of a partial vacuum; the surrounding air rushes in to fill the void, and by the collision of its particles produces the report. If the hydrogen be mixed with air, a similar but feebler explosion occurs when a lighted match is applied; hence it is especially necessary in all experiments with hydrogen to allow time for the expulsion of the atmospheric air from the apparatus before setting fire to the issuing gas. The explosion is most violent when 2 measures of hydrogen are mixed with 5 of air: if the mixture be diluted with a large excess either of hydrogen or of air, the explosion becomes more feeble; the heat evolved is less intense, and the combustion less sudden, until at a certain degree of dilution no explosion follows the application of flame, but the mixture burns slowly; whilst, if still more diluted, it takes fire only just at the spot where the heat is applied, but the combustion does not spread through the mass.

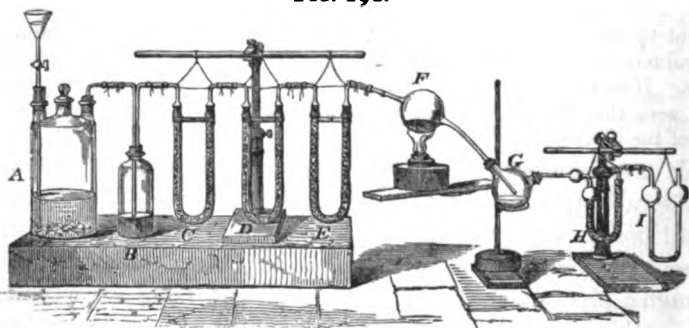
If a long tube, open at both ends, be held over a jet of burning hydrogen, a rapid current is produced through the tube, which occasions a flickering in the flame, attended by a series of small



explosions that succeed each other so rapidly and at such regular intervals as to give rise to a musical note, the pitch and quality of which varies with the length, thickness, and diameter of the tube.

Pure water may be formed in considerable quantities by a method differing from those hitherto described; the operation at the same time furnishes a means of ascertaining accurately the relative weights of oxygen and hydrogen which enter into the composition of water. It consists in transmitting a current of hydrogen over a weighed quantity of cupric oxide; at a red heat hydrogen deprives this oxide of its oxygen, and forms water: by determining the weight of the water thus produced, and the loss sustained by the oxide, the proportion of hydrogen which has combined with the oxygen can be ascertained. The apparatus required for the purpose is represented in fig. 292. A quantity of cupric

FIG. 292.



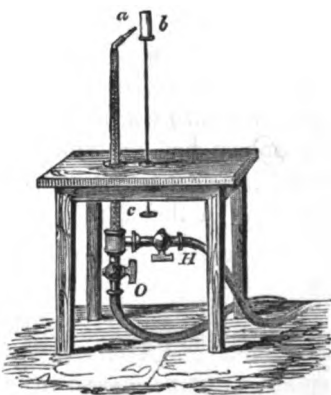
oxide is placed in the globe, *F*, which is constructed of glass of difficult fusibility, and the globe and its contents are then accurately weighed. A current of hydrogen, prepared from zinc and sulphuric acid in the bottle, *A*, is allowed to bubble up through a solution of potassic hydrate, *B*, and to traverse three bent tubes in succession; the first, *C*, is filled with fragments of pumice-stone moistened with a solution of corrosive sublimate ( $\text{HgCl}_2$ ); the second, *D*, contains fragments of fused caustic potash; and the third, *E*, is charged with pumice moistened with oil of vitriol. The mercuric salt and the potash remove the traces of arsenicum, sulphur, and carburetted compounds, which the gas might otherwise carry over, and the oil of vitriol absorbs the last traces of moisture. Perfectly pure and dry hydrogen gas is thus delivered in the globe, *F*. When all the air is completely displaced, heat is applied to the globe; the cupric oxide gives up its oxygen; water is formed, and becomes condensed in the receiver, *G*, as well as in the attached bent tube, *H*, which is filled with fragments of pumice moistened with oil of vitriol: the whole of the water formed is by this means arrested. *I* is a bulb tube containing a little oil of vitriol, which prevents the entrance of extraneous moisture, and by its motion shows the progress of the gas. When the globe, *F*, is cold, the hydrogen is displaced by a current of air, and on weighing the globe with the oxide after the experiment has terminated, the loss gives the quantity of oxygen which has combined with the hydrogen; whilst the difference between the amount of oxygen, and that of the water condensed in the receiver, *G*, and tube of acid, *H*, shows the quantity of hydrogen that has combined with it. Two grammes of hydrogen are in this manner proved to require exactly 16 grms. of oxygen for their conversion into water. (Dumas, *Ann. de Chimie*, III. viii. 189.)

Many other metallic oxides besides oxide of copper, when

heated in a current of hydrogen, part with their oxygen, and are brought back to the metallic condition. If the bulb be weighed first when empty, then when charged with oxide, and a third time after the stream of gas has been continued till all formation of water ceases, and till the tube has become cool, the loss of weight sustained by the oxide furnishes the proportion of oxygen combined with the metal. A true and very accurate analysis of the oxide will thus have been effected: 79.5 parts of cupric oxide are found in this way to contain 63.5 of copper and 16 of oxygen.

(347) Hydrogen in the act of combining with oxygen emits a very intense heat. By throwing a jet of oxygen into a flame of coal-gas or of hydrogen, or still better by introducing a jet of oxygen, as at *o*, fig. 293, into the centre of a jet connected at *H* with a gas-holder supplying hydrogen, so that the two gases may become mixed just before they issue from the common orifice of the tube *a*, a heat may be obtained which can scarcely be surpassed by chemical means. Sometimes the two gases are mixed in the proportion of 2 volumes of hydrogen to 1 volume of oxygen, and introduced into a bladder and burned as they issue through a tube of particular construction, known as Hemming's safety jet. It consists of a brass tube, about 6 inches or 15 centimetres long, and two-thirds of an inch (16<sup>mm.</sup>) in diameter, filled with pieces of very fine brass wire, which are packed closely together, and then wedged in very tightly by driving a stout conical piece of wire into the axis of the tube (492). This tube is supplied at one extremity with a blowpipe jet, and at the

FIG. 293.



other with a screw which can be connected with a stopcock adjusted to the neck of the bladder. The temperature produced by burning the mixed gases from such a jet is so intense that thick platinum wire is melted by it with ease, and is partially volatilized; iron and steel are melted, and burn with vivid scintillations. Rock crystal may be liquefied, and drawn out into threads like glass, and the stem of a tobacco pipe may be fused into an enamel-like bead. When the oxy-hydrogen flame, which is but very feebly luminous, is directed upon a small cylinder of lime, *b*, this earth does not fuse, but it becomes white hot, and then emits a very pure white light of great steadiness and intensity, which may be maintained for hours, if care be taken to expose to the flame fresh surfaces of the lime by causing it to revolve, continually but very slowly, by means of clockwork. This object may be obtained less perfectly by occasionally turning the pin, *c*, which supports the lime. Without this precaution a cavity would be formed opposite to the jet, from volatilization of a small quantity of the lime. This light was originally proposed by Lieut. Drummond, to be used in the trigonometrical survey of Great Britain, and when the rays are concentrated by a parabolic reflector it may be seen at very great distances. On the 31st December, 1845, it was seen across the Irish Channel, at half-past 3 P.M. (during daylight) from the top of Slieve Donard, in Ireland, by an observer

stationed at the top of Snowdon,—an interval of 108 miles in a direct line; and it has more than once been seen at a distance of 112 miles.

Water is formed abundantly whenever combustible bodies which contain hydrogen are burned with a free supply of air. Wood, tallow, oil, wax, alcohol, coal-gas, and most of our ordinary combustibles which burn with flame, in this manner furnish considerable quantities of water in the act of burning.

A striking experiment may be performed with hydrogen, which shows how purely conventional are the terms 'combustibles,' and 'supporters of combustion.' Let a tall bottle with a narrow neck be filled with hydrogen gas; through a cork which passes easily into the neck of the bottle fit a jet connected with a gas-holder containing oxygen; place the bottle mouth downwards and set fire to the hydrogen, then immediately insert the cork and jet, through which a stream of oxygen is gently issuing. The flame will appear to attach itself to the oxygen tube, and the jet of oxygen will be burning in an atmosphere of hydrogen. Combustion, in fact, occurs at the place where the two gases first come into contact. Suppose, for a moment, that the earth's atmosphere had contained hydrogen instead of oxygen; oxygen would have appeared to us in the light of a combustible gas, and hydrogen in that of a supporter of combustion.

## CHAPTER IV.

### CARBON—CARBONIC ANHYDRIDE—CARBONIC OXIDE.

#### § I. CARBONIC ANHYDRIDE, CARBONIC DIOXIDE, OR CARBONIC ACID: $\text{CO}_2 = 44$ .

*Atomic and Molecular Volume*,  $\square$ ; *Rel. wt.* 22; *Observed Sp. Gr.*, 1.529; *Theoretic Sp. Gr.*, 1.5203.

(348) AN atmosphere composed only of oxygen, nitrogen, and steam, though perfectly adapted to the support of animal life, would be unfit to sustain vegetation. Plants require for their growth and development a certain proportion of another gas—carbonic anhydride. Evidence of the existence of this body in the air (342) is easily obtained by exposing a saucer of lime-water to the atmosphere: in a few minutes its surface becomes covered with a thin pellicle, which if disturbed by agitation sinks to the bottom. The pellicle is renewed after each agitation until the whole of the lime contained in the liquid has been thus rendered insoluble. This white matter is chalk, which is formed

by the union of carbonic anhydride and lime. Such compounds of carbonic anhydride with bases are termed *carbonates*, hence chalk is chemically termed *carbonate of lime*, or *calcic carbonate*. When the chalk obtained is heated to bright redness (which, if the result is to be accurately examined, must be effected in a platinum tube), carbonic anhydride is expelled as a colourless and transparent gas, while pure quick-lime is left behind;  $\text{CaCO}_3$  becoming  $\text{CaO}$  and  $\text{CO}_2$ .

*Preparation.*—In actual practice, carbonic anhydride is obtained by a much more convenient plan. The carbonic being but a feeble acid, it is expelled from its compounds by almost every other acid which is freely soluble in water; it is therefore easily separated from its salts by the addition of one of these acids. Fragments of chalk, or of marble which is a more compact form of calcic carbonate, are placed in a retort or gas-bottle, and some powerful acid, such as the nitric or the hydrochloric, diluted with 8 or 10 times its bulk of water, is poured upon the chalk, when the acid exchanges its hydrogen for the calcium, producing calcic nitrate, or chloride, on the one hand, and carbonic acid ( $\text{H}_2\text{CO}_3$ ) on the other: the carbonic acid is so unstable that it immediately breaks up into water and gaseous carbonic anhydride, and this last escapes with a brisk effervescence. The following equation shows the nature of this decomposition when chalk and hydrochloric acid are employed;  $\text{CaCO}_3 + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$ .

Limestone, Iceland spar, oyster-shells, pearlash, sodic carbonate, and the carbonates generally, all yield carbonic anhydride when acted on by a strong acid.

*Properties.*—Under the ordinary pressure of the atmosphere carbonic anhydride is a colourless, transparent gas, with a faintly acidulous smell and taste; but when generated in a confined space in strong vessels it becomes condensed to a liquid as transparent and colourless as water, which, according to Regnault, boils at  $-109^\circ$  ( $-78^\circ \text{C.}$ ). At  $32^\circ$  ( $0^\circ \text{C.}$ ) it requires a pressure of 38.5 atmospheres to retain it in the liquid state (Faraday). It then has a specific gravity of 0.83, whilst at  $86^\circ$  ( $30^\circ \text{C.}$ ) the specific gravity is only 0.60. If these data be correct, the liquid expands by the application of heat four times more rapidly than air (Thilorier); but according to Andreeff (*Liebig's Ann.* cx. 10) the expansion of the liquid, although greater than that of the gas, is not so great as Thilorier states. Andreeff found the density of the liquid 0.947 at  $0^\circ \text{C.}$ ; 0.893 at  $10^\circ$ ; 0.86 at  $15^\circ$ ; and 0.779 at  $25^\circ \text{C.}$  Liquefied carbonic anhydride does not mix

freely with water, or with the fixed oils; but it is dissolved in all proportions by alcohol, ether, oil of turpentine, naphtha, and carbonic disulphide. When a stream of the liquefied body is allowed to escape into the air, it freezes into a snow-white solid (196): and if a tube containing liquid carbonic anhydride be plunged into a bath of the solid anhydride mixed with ether, and placed in the vacuum of the air-pump, the liquid in the tube will speedily be frozen into a clear, transparent, ice-like mass, which melts at  $-70^{\circ}$  ( $-57^{\circ}$  C.) The solidified anhydride is heavier than the liquid portion in which it is being formed.

Gaseous carbonic anhydride is not inflammable, neither will it support the flame of burning bodies: the extinction of a taper is one of the means frequently resorted to for detecting its presence. Many other gases, however, have the same property; some additional test, therefore, becomes necessary. Such a test is afforded by its action upon lime-water, which, when agitated with the gas, is immediately rendered milky from the formation of chalk; a few drops of any strong acid dissolve the chalk and restore transparency to the liquid; an excess of even carbonic acid has the same effect.

Carbonic anhydride in its concentrated form is irrespirable, for by producing spasm of the glottis it is prevented from entering the lungs; when diluted with air, however, it may be breathed without even a suspicion of its presence. If the proportion exceed 3 or 4 per cent. of the air it acts as a narcotic poison; and even in much smaller quantities its depressing effects are very injurious. It reduces both the frequency and power of the heart's action. The ill effects experienced in crowded and ill-ventilated rooms are partly due to the presence of this gas in undue quantity,\* but partially also to the accumulation of volatile putrescible organic particles given off from the surface of the lungs and skin. It is the combination of these circumstances which renders attention to ventilation a matter of such high importance.

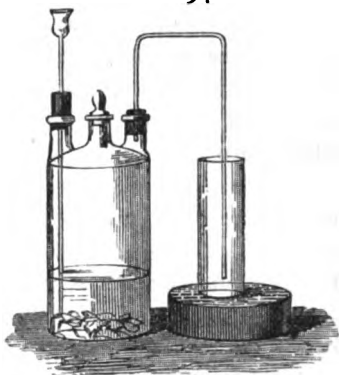
Gaseous carbonic anhydride is more than half as heavy again as atmospheric air; 1 litre at  $0^{\circ}$  C. and 760<sup>mm</sup>. weigh 1.977414

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\* The maximum observed by Roscoe in his experiments on the atmosphere of dwelling-houses, was 0.33 per cent., and this occurred in a crowded school-room. — (*Q. J. Chem. Soc.* x. 265.) Angus Smith found on the average, from the examination of 339 specimens of the air in mines, as much as 0.78 per cent.; and in several extreme cases it exceeded 2.0 per cent. The quantity of oxygen in the air of these mines gave an average of 20 per cent., but in some cases it fell as low as 18.6.

grm. (Regnault), or 100 cubic inches of it at 60° F. and 30 inches Bar. weigh 47.303 grains; from its density it may easily be collected in dry vessels by displacement, in the manner represented in fig. 294, and may be poured from one vessel into another like water.

FIG. 294.



No definite hydrated carbonic acid is known; the anhydride, both in the form of gas and in its denser conditions of liquid and solid, being, as its name indicates, free from water; but it appears to be convertible into a true acid by solution in water,  $\text{CO}_2 + \text{H}_2\text{O}$  yielding  $\text{H}_2\text{CO}_3$ . At the ordinary temperature, the gas is soluble in about its own bulk of water; and its solubility increases if the pressure be increased;\* but when the compression is suddenly removed, the gas escapes with brisk effervescence. Advantage is taken of this circumstance in the preparation of *soda-water*, as it is called. For this purpose the water, which may or may not contain soda or other substances in solution, is mechanically charged with a large quantity of carbonic acid, by the use of a condensing syringe, attached to a reservoir filled with the gas. The excess of the gas thus forced into the liquid occasions the agreeable briskness and pungency so much prized in this beverage.

A solution of carbonic acid in water reddens tincture of litmus; but the red colour disappears if the liquor be boiled for a few minutes, owing to the expulsion of the gas. The aqueous solution of the acid possesses solvent powers which, though in many instances extremely feeble, are yet far more extensive than those of pure water. By the continuous action of water charged with carbonic acid, even granite and the hardest rocks are disintegrated, few finely divided minerals being able to resist its gradual and long continued action. The proportion of gas dissolved is in many instances very minute, but as few natural sources of water exist which are not to a greater or less extent impregnated with carbonic acid, either by absorption from the atmosphere or from the soil, the solution, insignificant as it may at first sight appear, is continually pro-

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\* If the gas be simply transmitted through the water, the liquid seldom takes up more than two-thirds of its bulk.

ceeding, and in the lapse of time it effects changes of great importance and extent.

The briskness of spring water, and the preference given to it as a beverage, is partly occasioned by the carbonic acid which it contains; though its usual coolness and the abundance of atmospheric air dissolved in it are still more important. It is the absence of these qualities, combined with the presence of traces of organic impurities, which renders the taste of boiled or distilled water flat and mawkish (344 a).

Carbonic acid was originally termed *fixed air*, from the circumstance of its having been discovered by Dr. Black, in 1757, as a solid or fixed constituent in limestone, and from its becoming fixed or absorbed by solutions of the caustic alkalies.

(349) *Natural Sources of Carbonic Acid*.—Besides the processes for procuring the gas already described, there are a variety of cases in which it is produced on a very large scale in nature.

1.—Respiration in man and animals is always attended with the formation of a large proportion of the gas. This fact may be easily proved by forcing air from the lungs by means of a tube through lime-water, which will speedily become milky from the deposition of calcic carbonate. The proportion of carbonic anhydride in respired air varies from 3 to 4 per cent., being usually about  $3\frac{1}{2}$  per cent.

2.—Carbonic acid is also formed abundantly in the process of fermentation, and is the cause of the briskness in bottled beer, champagne, and other fermenting liquors. Many accidents have occurred from persons incautiously descending into an empty fermenting-vat before the gas has had time to escape and mix with the air: it is usual to facilitate the escape of the dense gas by leaving the plug at the bottom of the vessel open for some hours.

3.—In the operation of burning lime in the lime-kiln, the heat expels from the limestone the carbonic anhydride, which escapes in large volumes. Many a poor houseless wanderer, tempted by the warmth of the kiln, has lain down in the stream of air proceeding from it, and has slept to wake no more. By the operation of subterranean heat in volcanic districts upon limestone beneath the surface, large volumes of carbonic anhydride are continually finding their way into the atmosphere; immense quantities are discharged from open craters or from fissures and cavities in the soil; the springs in such districts are also frequently highly charged with it, and the gas escapes with effervescence when they reach the surface. The springs of

Seltzer, Pyrmont, and Marienbad, on the Continent, and of Tunbridge, in our own country, exhibit this phenomenon.

4.—The carbonic acid met with in spring water is in many instances derived from the gradual oxidation of the vegetable and other organic matter which it holds in solution, by the action of the oxygen of the air which all waters naturally contain. The lake waters from the primitive districts, such as those in the northern parts of Scotland, leave scarcely any residue on evaporation except a little organic matter; they are very free from carbonic acid, and the bulk of oxygen which they hold in solution is somewhat more than one-half that of the nitrogen. If such waters be kept in closed vessels for a few weeks in a warm room, the oxygen gradually decreases, and in its place a corresponding volume of carbonic acid is found. The pure water of Loch Katrine, for example, when first collected did not yield more than 0.22 cub. centim. per litre, or 0.06 cubic inch, of carbonic anhydride per gallon; but the quantity of this gas which the same sample yielded after it had been kept in a closed vessel for some weeks, in a warm room, rose to 1.34 c. c. per litre, whilst the oxygen had diminished to a similar extent. Spring waters which rise in a sandy district, the surface of which is sparingly clothed with vegetation, and from which consequently they can take up but little organic matter, contain but small quantities, often mere traces, of carbonic acid; whilst the springs of highly-cultivated districts, such as those which rest more or less directly upon the chalk, become charged with organic matter, which gradually undergoes oxidation in the soil, and the quantity of carbonic acid contained in such waters is always considerable, whilst the quantity of oxygen which they hold in solution is proportionately reduced.\* The extent to which this change takes

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\* The analysis of these gases or of any mixture of air with carbonic anhydride, such, for example, as respired air, may be effected with sufficient accuracy for most purposes in the following manner:—Supposing that the gas had been collected over either water or mercury, it becomes necessary to transfer a portion of it from the jar in which it has been collected to the one in which it is to be analysed. A method of effecting this is shown in fig. 295. Upon the board, *a d*, is fastened a pipette, designed for effecting this transfer; *a* is a cylindrical funnel of a capacity of about 30 cub. centim.; at *c* is a small steel or a glass stopcock, or a piece of vulcanized caoutchouc tubing compressed by a screw, which is simpler and less expensive; by either of these contrivances the contents of the funnel can be admitted to a wide thermometer-tube each portion of which must not be less than 30 centim. (12 inches) in length, which is furnished at *d* with a second screw clamp; *b* is a bulb of the capacity of about 16 c. c. (1 cub. in.); from the upper part of *b* proceeds another piece of thermometer-tube, bent as shown in the figure, to allow of its introduction into the gas-jar; this bent

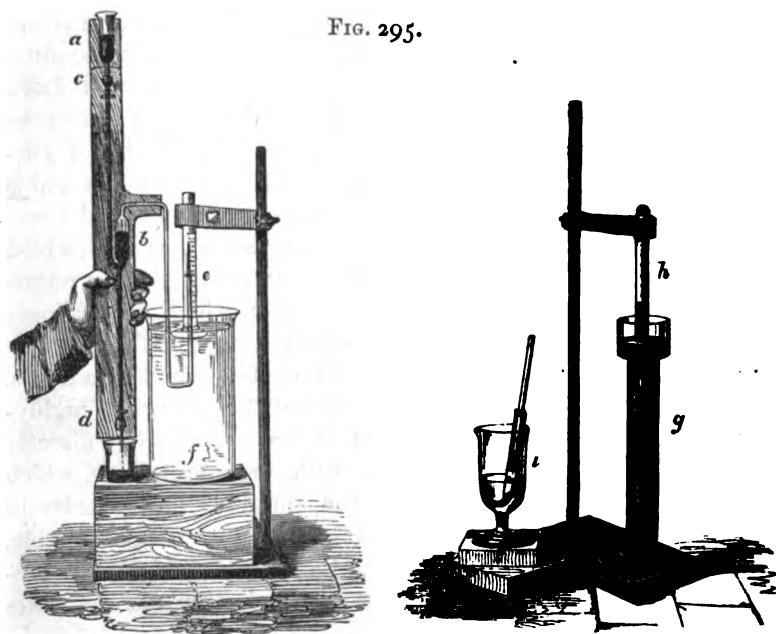


place in river water is very remarkable. It is well exhibited in the case of the Thames.

On one occasion, some samples were taken from the river at low water at different points on the same day, in August, 1859; those collected above the metropolis being nearly free from contamination with sewerage products, whilst those obtained lower down were extensively impregnated with them. The gases were expelled from each sample by boiling, within twenty-four hours from the time of its collection, and the results obtained are given in the following table, in which they are contrasted with the proportions of each gas furnished by a

portion may be connected to the bulb *b* with a flexible joint of caoutchouc tubing, by which the manipulation of the instrument is facilitated. To use the instru-

FIG. 295.



ment, the funnel, *a*, is filled with mercury, the stopcocks are both opened, and as soon as the air has been displaced from the vertical portion of the fine tube, and mercury escapes through *d*, the lower stopcock is closed; the mercury quickly displaces the air from the rest of the tube, and from the bulb *b*, and as soon as it begins to flow out at the open extremity of the recurved portion, the stopcock, *c*, is closed. The instrument being now full of mercury is introduced into the jar, *e*, of the gas to be transferred, and its open extremity is raised above the level of the water in the jar, *e*; the stopcock, *d*, is then opened, and whilst the mercury runs out into a vessel placed for its reception, the gas enters from *e*, and occupies the place of the mercury in the bulb, *b*. When a sufficient quantity has been admitted, the tube is depressed below the level of the water in the jar, *e*; the stopcock, *d*, is closed, and the pipette, which is sealed by the admission of a little water into the capillary tube, is withdrawn from the jar, *f*. The gas can now be transferred to the graduated tube, *h*, standing in the jar of mercury, *g*; the bent limb of the pipette is introduced into the tube, *h*, which has been pre-

similar experiment upon a sample of river water taken above Teddington Lock, where it was in a pure condition.

Temp. of river, 21°·5 C. 70° F.	Kingston.	Hammer- smith.	Somerset House.	Greenwich.	Woolwich.	Erith.
Total quantity of gas in cubic in. per gallon . . .	14·67	{ Not deter- mined. }	17·49	19·77	17·50	20·64
Carbonic anhydride . . .	8·42	{ Not deter- mined. }	12·56	15·43	13·40	15·80
Oxygen . . . . .	2·07	1·16	0·43	0·07	0·07	0·52
Nitrogen . . . . .	4·18	4·24	4·50	4·28	4·03	4·32
Proportion of Oxygen to Nitrogen . . . . .	1 : 2	1 : 3·7	1 : 10·5	1 : 60	1 : 52	1 : 8·1

From these experiments it will be seen that the water from Kingston (above Teddington) is thoroughly aerated, and contains oxygen in the proper proportion to the nitrogen, which when in solution is as 1 to 2. At Hammersmith, the effect of the organic impurities in abstracting the oxygen begins to be evident. It is much more marked at Somerset House, whilst at Greenwich, where the condition of the river at low water is about at the worst, the oxygen has nearly disappeared. At Woolwich, it is nearly as bad, but by the time Erith is reached a great improvement is perceptible. Had the experiments been continued still lower down the river, the proportion of oxygen would have continued to increase,

viously filled with mercury. Fresh mercury is poured into the funnel, *a*, of the pipette, and on opening the stopcock, *c*, the gas is expelled into the tube, *k*; the gas should not occupy more than two-thirds of the capacity of this tube.

The proportions of carbonic anhydride, of nitrogen, and of oxygen are now easily ascertained in the following manner:—The bulk of the gas in the tube, *k*, is to be carefully read off, care being taken to bring the mercury to the same level within and without the tube; the temperature and the pressure being observed as usual. Supposing that it has thus been ascertained that a bulk of gas of about 8 or 10 cub. centim. is to be subjected to the analysis, the operator, by means of a glass syringe, or a small glass pipette with a recurved tube, throws up ten or twelve drops of a solution of caustic potash (sp. gr. 1·4) into the tube. The glass syringe may be extemporaneously prepared from a strong tube which is softened in the flame of a lamp, drawn off and recurved at one end, as shown in the figure at *i*; this constitutes the body of the syringe, whilst the piston is easily formed of a piece of glass rod, provided with a plug of caoutchouc.

The operator then agitates the contents of the tube by rapidly thrusting down the tube into the mercury, and withdrawing it, taking care to keep the mouth below the surface of the mercury: this manoeuvre is several times repeated in quick succession; the tube is again left at rest for a minute or two, and the absorption is noted by a second time reading off the volume of the gas at the proper level. The difference indicates the amount of carbonic anhydride.

In order to ascertain the proportion of oxygen in the remainder, the plan recommended by Liebig is the simplest:—A solution of 1 part of pyrogalllic acid in 6 of water is prepared, and about 40 drops of the solution is by a *fresh* pipette injected into the tube *k*, and the mixture is briskly agitated as before; the solution of potash, if oxygen be present, becomes of an intense bistre colour, and the oxygen is quickly and completely absorbed; the gas is measured a third time, and the residue is estimated as nitrogen; the difference between the second and third readings giving the volume of oxygen. A small quantity of carbonic oxide amounting to between 2 and 3 per cent. of the volume of the oxygen is always formed in this operation.—(Crace Calvert; Boussingault.)

owing to the admixture of aerated sea-water and the absorption of oxygen due to the successive exposure of the water to the air in its onward flow.

5.—Carbonic anhydride is one of the principal constituents of what is termed *choke-damp* by miners, and it often occasions much loss of life after the occurrence of an explosion of carburetted hydrogen, or *fire-damp*. It also accumulates frequently in the old workings of mines, and in pits or wells. Before descending into them, it is usual to lower a lighted candle in order to ascertain whether the light will burn; if it does so, it is generally considered safe to venture down. Instances, however, are on record in which a candle was found burning in an atmosphere which, notwithstanding, contained sufficient carbonic anhydride to cause death. When it is necessary to enter into an atmosphere considerably charged with this gas, Graham suggests as a precaution that the mouth and nostrils be covered with a cloth containing a mixture of slaked lime and crystallized sodic sulphate. Such a mixture is porous enough, in a layer of 25<sup>mm</sup>. or an inch thick, to allow the passage of sufficient air for respiration, whilst the moist lime completely absorbs the carbonic anhydride.

6.—There is also another mode in which carbonic anhydride is very largely formed, which, independently of its importance as a source of the gas, is interesting as throwing light upon its chemical nature. Whenever charcoal, or bodies which, like wood, coal, oil, or tallow, contain carbon, are burned either in oxygen or in air, carbonic anhydride is obtained abundantly; if the gas, after combustion has terminated, be agitated with lime-water, this liquid will be immediately rendered milky. According to Angus Smith, two candles in burning may be estimated to produce about as much carbonic anhydride as one man would emit by respiration during an equal interval of time, or about 1260 cubic inches (20.6 litres) per hour.

Carbon may again be extracted from carbonic anhydride. If a small piece of potassium, heated till it begins to burn in the air, be introduced by means of a platinum spoon into a jar of gaseous carbonic anhydride, the potassium will continue to burn with great brilliancy. Potash will be formed at the expense of the oxygen which the gas contains, whilst charcoal is liberated, as may be seen in the black particles which are suspended in the water into which the spoon is plunged after the combustion is complete. Thus carbonic anhydride is shown, both synthetically and analytically, to be a compound substance, consisting of carbon and oxygen, and its composition may be represented as follows:

Carbon	C	=	By weight, 12 or 27·28	Dumas, 27·28	By vol. 2 or 1·0?	=	Sp. gr. 0·4146
Oxygen	O <sub>2</sub>	=	32 72·72	72·72	2 1·0	=	1·1057
<hr/>							
Carbonic anhydride	{ CO <sub>2</sub> =		44 100·00	100·00	2 1·0	=	1·5203

Carbonic anhydride is not decomposed by such elevation of temperature as we can obtain in our furnaces, but if a succession of electric sparks be transmitted through the gas it is partially separated into carbonic oxide, and free oxygen. Sulphur, chlorine, and the halogens may be heated with the gas without decomposing it; but if heated with hydrogen, water and carbonic oxide are formed, the decomposition being represented thus,  $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$ . Carbon, and many of the metals, such as iron and zinc, also remove a portion of the oxygen from the carbonic anhydride, and convert it into carbonic oxide (357).

*Applications.*—Sir G. Gurney has turned the property of extinguishing flame possessed by carbonic anhydride to an important practical account. Coal mines, at different times and from various causes, are liable to take fire, and from the vast mass of heated matter, the conflagration not unfrequently resists all the ordinary means of checking its ravages; many acres of subterranean fire are thus produced, and the workings are of necessity abandoned. Sir G. Gurney, in such cases, closes every opening into the mine but two, one for the entrance, the other for the escape of the gases, and then, by the agency of the steam jet, pours into the mine a current of impure carbonic anhydride and nitrogen, obtained by forcing a stream of air through a coke furnace into the mine, so as to fill the entire workings with the gas; he has thus on several occasions succeeded at a very small expense in extinguishing fires which have raged unsubdued for years.

A very remarkable case of this kind was mentioned in the *Times* for May 22, 1851:—The ‘burning waste of Clackmannan,’ situate about seven miles from Stirling, had been for 30 years on fire. It occurred in a seam of nine-foot coal, and extended over an area of 26 acres; yet the fire was successfully extinguished:—about 8,000,000 cubic feet, or 226,500 cub. metres, of gas were required to fill the mine, and a continuous stream of impure carbonic anhydride was kept up night and day for about three weeks. The difficulty lay not so much in putting out the fire, as in cooling down the ignited mass so that it should not again burst into flame on readmitting the air. In order to effect the necessary reduction of the temperature, water was blown in along with the carbonic anhydride in the form of a fine spray or mist. Subsequently, cold air mixed with the spray was blown in, and in a month from the commencement of operations the fire was found to be completely extinguished.

(350) *Carbonates.*—Though but a feeble acid, carbonic acid forms a numerous and important class of salts, which has till

lately been regarded as monobasic; but there can be no doubt that it ought, in accordance with recent usage, to be considered as dibasic (554).

The carbonates, with the exception of those of the alkali-metals, are not soluble in water; but many of the insoluble carbonates, and in particular those of calcium, magnesium, barium, and strontium, may be dissolved to some extent by water charged with carbonic acid, and are deposited in a crystalline form as the gas escapes slowly from the liquid. All the carbonates are dissolved with effervescence by diluted nitric acid, and even by acetic acid: the gas which comes off is colourless, and renders lime-water turbid; it possesses the properties of carbonic anhydride, above described. The most delicate test of the presence of free carbonic acid is one of the basic salts of lead, such as the subnitrate or the subacetate, a solution of which is instantly rendered milky by the action of a solution of carbonic acid upon it. The carbonates of the alkali-metals, when in solution, are also decomposed by acids, with effervescence; they give with salts of calcium a white precipitate, which is immediately redissolved by an acid, with effervescence. All the carbonates, with the exception of those of the alkali-metals and of barium, are decomposed by prolonged ignition, the salt being decomposed into the anhydride and a metallic oxide. The carbonates have considerable tendency to combine with each other, and form double salts, like dolomite, which is a double carbonate of calcium and magnesium ( $\text{MgCa}_2\text{CO}_3$ ). Many basic carbonates are also known: they are often hydrated compounds—such, for example, as malachite ( $\text{CuH}_2\text{O}_2, \text{CuCO}_3$ ).

If M and M' represent the atom of any two different metallic monads, such as potassium and sodium, the general formulæ of the carbonates will be thus indicated:—

Normal salt,  $\text{M}_2\text{CO}_3$   
 Acid salt,  $\text{MHCO}_3$   
 Double salt,  $\text{MM}'\text{CO}_3$

The following table represents the composition of some important carbonates:—

Potassic carbonate	...	...	...	...	...	$\text{K}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
Sodic carbonate	...	...	...	...	...	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
Potassio-hydric carbonate (bicarbonate)	...	...	...	...	...	$\text{KHCO}_3$
Sodio-hydric carbonate (bicarbonate)	...	...	...	...	...	$\text{NaHCO}_3$
Trona (sodium sesquicarbonate)	...	...	...	...	...	$2\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$
Ammonic sesquicarbonate	...	...	...	...	...	$2[(\text{H}_4\text{N})_2\text{CO}_3] \cdot \text{CO}_2$
Baric carbonate	...	...	...	...	...	$\text{BaCO}_3$

Calcic carbonate	...	...	...	...	...	...	CaCO <sub>3</sub>
Magnesian carbonate	...	...	...	...	...	...	MgCO <sub>3</sub>
Dolomite	...	...	...	...	...	...	MgCa <sub>2</sub> CO <sub>3</sub>
Baryto-calcite	...	...	...	...	...	...	BaCa <sub>2</sub> CO <sub>3</sub>
Malachite	...	...	...	...	...	...	CuCO <sub>3</sub> , CuH <sub>2</sub> O <sub>2</sub>
Blue carbonate of copper	...	...	...	...	...	...	2CuCO <sub>3</sub> , CuH <sub>2</sub> O <sub>2</sub>

## § II. CARBON : C=12.

*Sp. Gr. as diamond, 3·33 to 3·55 ; Vapour Density unknown ;  
Dyad in CO ; usually Tetrad, as in CO<sub>2</sub>, and CH<sub>4</sub>.*

(351) CARBON is an elementary body of the greatest importance. It is found nearly in a state of purity in the diamond ; with a larger proportion of foreign admixture it occurs in the form of graphite, and still less pure in the abundant deposits of pit coal. It is also met with in enormous quantities in combination, under a variety of forms. Independently of the quantity of it which exists diffused through the atmosphere in the state of carbonic anhydride, it is a component of the numerous varieties of calcic and of magnesian carbonate, constituting nearly an eighth of the entire weight of calcic carbonate, and more than a seventh of that of magnesian carbonate. It is the characteristic ingredient of all substances which are termed *organic*—that is, of substances which are produced directly or indirectly from the vegetable or animal creation. The solid parts of plants, shrubs, and trees owe their form and solidity to this element, which is mainly supplied to them from the carbonic anhydride in the atmosphere. This action of plants upon carbonic anhydride is one of the means ordained for preserving uniformity in the composition of the air. The quantities of carbonic anhydride poured forth from the bowels of the earth, and derived from the processes of respiration and combustion, and from numerous other less apparent sources, would by degrees occasion an injurious accumulation of the gas, but for this compensating action. In solar light the leaves of plants decompose both carbonic anhydride and water, appropriating the carbon and the hydrogen of each for their own growth and nutrition, whilst a large proportion of the oxygen which these compounds contained is returned into the air in the gaseous state. The carbonic anhydride thus poured out by animals as a refuse and poisonous product, supplies food and sustenance to the vegetable world, which in its turn converts the carbon into a form suitable for the maintenance of life in animals. Each great division of animated nature is thus seen to be essential to the well-being and even to the support of the other. The fuel

which has been burned and dissipated in vapour is again reduced to the solid state, and by the agency of vegetable life it is once more fitted for combustion and made a depository of fresh energy derived from the sun. Plants are, in fact, the grand agents by which, under the influence of the chemical actions of the sun's rays, deoxidation is effected, while animals are the channels through which recombination with oxygen is unceasingly produced.

(352) *Diamond, Sp. Gr.* from 3.33 to 3.55.—Carbon is found in its purest state in the *diamond*, which occurs crystallized in forms belonging to the regular system. These crystals are generally derivatives from the octohedron, with a cleavage parallel to each of the planes of the octohedron; the faces are often convex, and the edges are generally rounded, or *lenticular*, as they are termed, in such crystals. Diamonds usually present themselves under the appearance of semi-transparent rounded pebbles, enclosed in a thin brownish opaque crust. The gem, when freed from this coating, is generally colourless; such specimens are the most prized; it is, however, met with of various tints, the more common of which are yellow and different shades of brown. The most famous diamond mines are those of Golconda and Bundelcund in India, of Borneo, and of the Brazils. The origin of the diamond is entirely unknown; it is not probable that it has been formed by crystallization after fusion, since intense heat reduces the diamond to the form of graphite. The circumstances under which diamonds are found in nature afford no clue to the process of their formation. They have been found imbedded here and there in a fine-grained quartzose rock (*Itacolumite*) in Brazil, but with few exceptions the gem is found scantily in an alluvial matrix, consisting chiefly of sandstone and rolled quartz pebbles, from which the diamonds are extracted by washing and careful sorting.

Diamond is the hardest body known, crystallized boron approaching it most nearly in this respect: it is cut and polished by employing its own powder for the purpose. The fine diamond dust used for this object, after mixture with a little olive oil, is spread over a revolving steel plate, and the diamond, cemented into a suitable support, has each of its faces in turn presented to the flat face of the disk.

The Kohinoor diamond, which was cut in 1852, for the Queen, was imbedded in a copper vessel of about the size of a teacup, into which it was cemented with a mixture of equal parts of tin and lead. When it was necessary to change the position of the gem, the solder was softened by immersing the cup, with the diamond imbedded, in a charcoal fire, and heating the metal till it assumed a consistence resembling that of wet sand; in order to cool the diamond

more quickly, it was plunged first into warm water and then into cold water; the cutting was effected by means of a cast-iron wheel revolving on a vertical axis about 2400 times per minute; the diamond rested upon the upper surface of the wheel, being held in its position by a kind of vice, and the pressure against the revolving disk was increased or diminished by adding or removing weights. From time to time the face of the diamond was touched with a hair pencil dipped in a cream of diamond dust and oil.

The most important use to which the diamond is applied is the cutting of sheets of glass: only the natural face of the crystal can be employed for this purpose, crystals with curved faces being the best; they are set in a convenient handle; in cutting, a line is traced with the diamond across the glass in the proper direction; slight pressure on each side of the cut then determines the fracture in the right direction. A true cut is effected by such a diamond if properly used, whilst a diamond with angles obtained by cleavage produces only a superficial scratch with ragged edges.

The diamond has a very brilliant lustre and a high refracting power; it is a non-conductor of electricity. After exposure to sunshine, many specimens emit a feeble phosphorescent light, which may be seen in a darkened room. In vessels from which air is excluded, it may be heated intensely without change. If it be suspended in a cage of platinum wire, heated to bright redness, and plunged into oxygen gas, it will burn with a steady red light, and with the production of pure carbonic anhydride. The diamond, however, is not perfectly pure carbon: it always leaves a minute yellowish ash, which has been found to contain silica and ferric oxide. This ash has generally the form of a cellular network, and may perhaps, at some future time, assist in determining the origin of this valuable gem. No heat hitherto applied suffices for the fusion or volatilization of the diamond, or indeed of carbon in any of its forms, though in the intense heat of the voltaic arc, it appears to be mechanically transported from one electrode to the other (280). When the diamond is introduced into the flame of the voltaic arc, it undergoes a remarkable change; as soon as it becomes white hot it begins to swell up, loses its transparency, suddenly acquires the power of conducting electricity, becomes specifically lighter, and is converted into a black opaque mass, resembling coke. The density of a diamond thus altered was 2.6778; while in its crystalline condition it was 3.336 (Jacquelin, *Ann. de Chimie*, III. xx. 467). The heat of the oxyhydrogen jet was found to be insufficient to produce this change.

(353) *Graphite*, or *Plumbago* (*Sp. Gr.* from 2.35 to 2.15) is a second form in which carbon occurs native. Its once celebrated mine at Borrowdale is now nearly exhausted. It is likewise found in Ceylon, and in several parts of the United States, always in rocks belonging to the earliest formation. It has also



been met with abundantly in the Batougal mountains, near the frontier of China, in South Siberia. The Borrowdale graphite occurs in clay-slate; in other localities it is imbedded in gneiss, mica-slate, or granular limestone. Graphite occurs either massive or in six-sided crystalline plates belonging to the rhombohedral system. Carbon, in the two forms of diamond and plumbago, offers an excellent instance of dimorphism; the properties which it displays in these two states are as widely different as those of any two dissimilar elements. Graphite has a metallic, leaden-grey lustre, whence its familiar name of *black-lead*. It is very friable, and consequently feels unctuous to the touch, and leaves traces on paper upon which it is rubbed. The particles of which it is composed are, however, extremely hard, and they rapidly wear out the saws employed to cut it. It appears to exist in two distinct modifications, one of which, like the Borrowdale graphite, is fine-grained and amorphous; the other, like the Ceylon variety, is composed of small flat plates, united by a cementing material; this form of graphite generally occurs in a matrix of quartz (Brodie). Graphite is an excellent conductor of electricity. It is never met with in a state free from foreign admixture: when burned in oxygen it leaves from 2 to 5 per cent. of ash, which generally contains quartz, and oxides of manganese and iron; these bodies, however, are merely accidental impurities. The fine-grained amorphous graphite is highly prized for the manufacture of 'lead pencils': where pieces of sufficient size can be obtained they are sawn into thin slices, and these again into small rectangular prisms, which are placed in cedar wood for use. It has been found that the smallest fragments, if of good quality, and the fine powder, may be again reduced into coherent plates by subjecting it to enormous pressure, and may thus be fitted for the manufacture of the best pencils. Black-lead is extensively used for the lubrication of machinery, and as it is quite unaltered by exposure to the weather, it forms a serviceable coating to protect coarse iron work from rust. An application of graphite which is of some importance to the chemist, is its use in the manufacture of what are termed black-lead crucibles, or blue-pots; the clay employed in making them is mixed with a coarse kind of graphite; the pots made from this mixture are much less likely to crack when heated than if made of fire-clay only.

Brodie (*Ann. de Chimie*, III. xlv. 351) has described a method of obtaining graphite in a state of purity, and in a very finely divided form. It consists in mixing coarsely-powdered graphite with a fourteenth of its weight of potassic chlorate; the mixture is introduced into an iron pot, and diffused through a

quantity of concentrated sulphuric acid, equal to twice the weight of the graphite employed. The mixture is heated over a steam bath so long as any peroxide of chlorine is disengaged: it is then allowed to cool, thrown into water, and washed thoroughly. If graphite which has been subjected to this treatment and dried, be heated to redness, it gives off gas, increases greatly in bulk, and becomes reduced to an exceedingly fine powder. In cases in which the graphite was originally mixed with silica, this impurity may be got rid of by adding a small quantity of sodic fluoride to the mixture of graphite with potassic chlorate and sulphuric acid; the silica is then expelled in the form of silicic fluoride.

It appears that during this treatment the graphite becomes oxidized; and that a new compound of carbon, hydrogen, and oxygen is formed, which enters into combination with the sulphuric acid,\* and this compound is decomposed by ignition.

The graphitic modification of carbon may be obtained artificially by several processes. When cast iron is melted in contact with an excess of charcoal, it takes up a considerable quantity of it, and if the iron be allowed to cool slowly, the carbon crystallizes out in the six-sided plates peculiar to graphite. In the manufacture of coal-gas, those parts of the retort which are exposed to the highest temperature, partially decompose the gas as

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\* This oxidized substance may be obtained in a state of purity by the following process (*Q. J. Chem. Soc.* xii. 261):—Mix intimately 1 part of finely powdered Ceylon graphite with three parts of potassic chlorate, and add sufficient of the strongest nitric acid to render the mixture fluid; after which expose it for three or four days to the heat of  $140^{\circ}$  ( $60^{\circ}$  C.), on a water bath.\* Exposure of the mixture to the direct rays of the sun abridges the time required. The residue must be washed with water freely, dried, and subjected four or five times to the same treatment.

*Graphitic Acid* ( $C_{11}H_4O_4$ ), as this compound is termed by Brodie, forms yellow silky plates, which are insoluble in water and in acids. It is slowly attacked by ammonia and by potash, the ammonia gradually combining with it, forming a gelatinous body susceptible of decomposition by acids, which occasion the separation of a white gelatinous mass.

When graphitic acid is exposed to a temperature of between  $500^{\circ}$  and  $600^{\circ}$  ( $260^{\circ}$  and  $320^{\circ}$  C.), it undergoes decomposition with almost explosive violence, with evolution of heat and light, giving off gas, and producing an exceedingly bulky, flocculent, sooty-looking substance which still retains both carbon and hydrogen. If, in order to regulate the heat applied, the graphitic acid be placed in paraffin oil, and the temperature be gradually raised to  $270^{\circ}$  C., the hydrocarbon becomes of a deep red colour, and the acid gives off water and carbonic anhydride, leaving a substance of graphitoid appearance, consisting of  $C_{22}H_2O_4$ ; if this new body be further heated in an atmosphere of nitrogen, water and carbonic oxide escape, leaving a residue containing  $C_{10}H_4O_{11}$ . Even if heated to redness in nitrogen, it retains a portion of oxygen and hydrogen, giving off water, carbonic anhydride, and carbonic oxide.

Brodie considers that in these compounds the graphite retains its allotropic state, which he terms *Graphon*, and that it possesses in this form a combining number of 33, with the symbol Gr. If this be so, graphitic acid  $C_{11}H_4O_4$  might be represented as  $Gr_3H_4O_4$ , the first residue  $C_{22}H_2O_4$  as  $Gr_2H_2O_4$ , and the second  $C_{10}H_4O_{11}$  as  $Gr_{10}H_4O_{11}$ ; graphitic acid being regarded by Brodie as analogous to the hydrated oxide of silicon  $Si_2H_4O_4$ , discovered by Wöhler and Buff (471a.)

it escapes; a part of the carbon which it held in combination is deposited, and by degrees a layer of very pure dense carbon is formed, possessed of a lustre resembling that of a metal. The density and appearance of this mass vary according to the temperature, and the gaseous pressure to which it has been subjected.

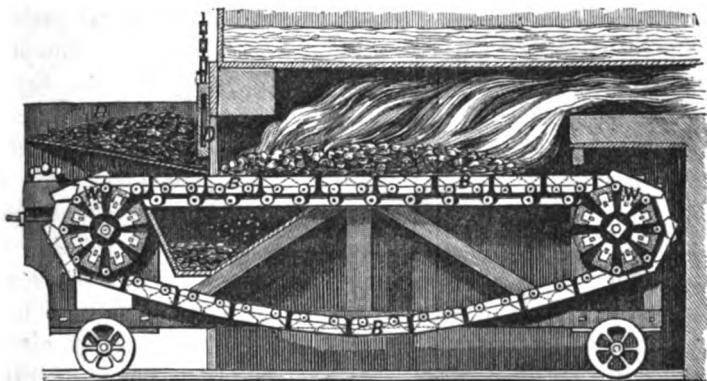
*Pit coal* is a substance originally of vegetable origin, which has become altered in appearance and composition by the combined action of heat and moisture under great pressure. The composition of coal varies considerably according to the extent to which these decomposing actions have advanced: the different varieties of coal will be noticed hereafter, but in all cases it consists, like vegetable matter in general, of carbon, hydrogen, and oxygen, with a small proportion of nitrogen; and in addition, it contains a variable quantity of saline and earthy substances, which always exist in the juices of plants, besides a variable amount of iron pyrites or ferric disulphide ( $\text{FeS}_2$ ). These saline matters are left, when the coal is burnt in an open fire-place, and constitute the ashes; whilst the carbon and hydrogen are entirely converted into carbonic anhydride and water, if an adequate supply of oxygen from the air be furnished: but the burning of coal, even in an open fire, is never complete, so that it gives off a quantity of gaseous and tarry matters, holding finely divided carbon or soot in suspension.

(353a) *Consumption of Smoke*.—When a quantity of fresh coal is thrown upon a hot fire, the coal immediately begins to undergo decomposition; various compounds of carbon with hydrogen being abundantly extricated in the form of gas or vapour: a portion of these hydrocarbons immediately takes fire and burns with a bright, luminous flame, but a large proportion of these bodies, on coming into contact with the glowing embers, is further more or less completely decomposed, the carbon and hydrogen experiencing a separation from each other; the hydrogen, which is the more combustible element, becomes burned, or, if the supply of oxygen be inadequate, it passes off in the gaseous form, whilst the carbon, owing to the minute state of subdivision of its particles, is carried up the chimney suspended in the current of heated gases. By proper care, the volumes of black smoke ordinarily poured forth from the chimneys of our houses and factories, may, however, be prevented, and the annoyance due to this contamination of the atmosphere in our large towns to a great extent obviated; whilst a considerable saving of fuel may at the same time be effected.

The principles involved in the prevention of smoke are—1st, the supply of fuel in small quantity at a time, taking care to maintain a strong, steady fire, in order that the gases may be burned as fast as they are generated; and, 2nd, the supply of an adequate quantity of atmospheric air. The latter condition is not so easily accomplished in the furnaces of the manufacturer as might be supposed. The regulated supply of fuel in small quantities may obviously be ensured by due care on the part of the stoker, but it requires more labour and attention than is usually bestowed by him. Various contrivances have been from time to time invented for effecting the prevention of smoke, one class of these having for

their object the regular supply of fuel by mechanical means, as is proposed by Juckes's apparatus, the essential points of which are shown in section in fig. 296.

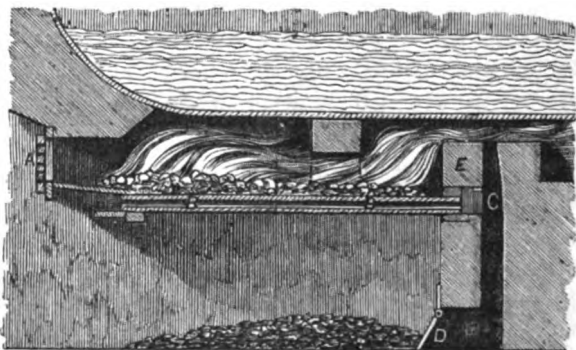
FIG. 296.



The fire-bars, B B, in this case consist of a series of endless chains, which are carried very slowly forward by machinery connected with the toothed wheels w, w. A continuous but very gradual supply of fuel is furnished from the hopper, H, in front of the furnace, and the amount of coal thus admitted is regulated by raising or lowering the door D. This apparatus fulfils its object well, but the wear and tear of the fire-bars is considerable.

In another class of smoke-burning contrivances, the object is to burn the smoke which is formed in small quantity, by supplying air at a high temperature to the unburnt gases as they escape from the fire-place. Fig. 297 represents in section the plan adopted by Mr. F. C. Hills for attaining this object.

FIG. 297.



The coal is thrown into the fire by hand, but in moderate quantities at a time; the fire-door, A, being perforated for the admission of air. The fire-

bars, B B, are tubular, and allow the passage of air into the channel, c, which opens into the chimney just behind the bridge, E, of the fire-grate; the air becomes heated as it passes through the tubular bars, and, if the quantity thus admitted is not sufficient to complete the combustion of the unburned gaseous products as they escape, more air can be supplied from below by raising the damper, D.

(353 b) *Coke*.—When the coal is heated in long closed iron cylinders, so constructed as to exclude atmospheric air, but to allow free escape for volatile matters, a large quantity of gaseous

substances, containing the oxygen, hydrogen, and nitrogen, with a part of the carbon of the coal, passes off, while the greater proportion of the carbon remains behind, and constitutes *coke*, which is the only one of the products that will be noticed at present. Coke is, chemically, the same substance as the graphite deposited from the gas, but in a less pure form, owing to the earthy matters which are mixed with it. As a fuel coke is often to be preferred to coal, since it burns without emitting any visible smoke; it has also the advantage of not swelling or caking together when heated, and thus the danger of choking the draught is avoided. The higher the temperature to which coke is exposed during its manufacture, the more dense does it become, and the better is it fitted for producing a steady and intense heat, when burned as fuel; though unless the supply of air be tolerably abundant, it burns less freely in this dense condition than when less compact. In order to furnish a coke suited for the use of locomotive engines, it is customary to construct coke ovens, which are usually built of brick, and lined with fire-bricks, the walls being from 2 to 3 feet (6 to 9 decimetres) in thickness, to economize heat: and this object is further effected by building several ovens together in one continuous piece of masonry. One of these ovens, 12 feet (3·7 metres) in internal diameter and 4 feet (1·24 metres) in height, will convert  $3\frac{1}{2}$  tons (or about 3500 kilog.) of coal into coke in forty-eight hours. The oven has a sliding door in front, for the purpose of introducing and withdrawing the charge, and for regulating the admission of air, which plays over the surface of the heap and burns off the volatile matters before their escape by a short chimney. The combustion proceeds gradually, from above downwards: in about forty hours after commencing the operation, the door is completely closed, and the furnace left for five or six hours; at the end of that time the coke is withdrawn and quenched with water. A bituminous coal, like the Newcastle coal, furnishes in this way a very dense lustrous coke, which splits into long columnar masses or prisms, as the temperature in the oven gradually falls when the door is closed. A fresh charge is introduced into the oven while its walls still remain red hot. The coke is never melted in this operation, and the appearances of fusion which it frequently exhibits are due to the liquefaction, by heat, of the bituminous portions of the coal, before they have undergone carbonization. A very pure form of carbon is frequently observed in the fissures of the mass, in the form of black fibres, closely resembling horsehair in appearance.

Coke may also be prepared, though with less advantage, by a smothered combustion of the coal in heaps, in a manner similar to that practised in making charcoal. Coke is subject to great variation in appearance and bulk, this variation depending on the kind of coal employed in producing it: it is, however, nearly always more bulky than the coal that yields it.

(354) *Charcoal: Amorphous carbon.*—Carbon also exists in a third form, distinct from that of graphite, and in this state it is amorphous, or entirely destitute of crystalline structure. *Lamp-black* is a variety of this kind of charcoal; it is largely manufactured by heating, in an iron pot, vegetable matters rich in carbon, such as resin or tar; the vapours thus disengaged are kindled, and burned in a current of air insufficient for their complete combustion; the hydrogen which these bodies contain, being the more inflammable ingredient, burns off first, leaving the carbon in the form of a very finely-divided powder, such as that which constitutes the visible portion of smoke. The smoky products of this imperfect combustion are made to pass through a large chamber, the walls of which are covered with coarse cloth, and here the lamp-black is deposited. Lampblack always retains a portion of some incompletely burned compounds of carbon and hydrogen. The purest form in which finely divided carbon can be obtained for chemical purposes is furnished by passing the vapour of oil of turpentine or of ether slowly through tubes maintained at a full red heat; a fine powder of charcoal is deposited within them; but this, also, even if again heated intensely in closed vessels, always retains traces of hydrogen.

Tinder is another variety of carbon in the amorphous or non-crystalline form; but the most important variety is *Wood Charcoal*, which is largely manufactured by heating billets of wood to dull redness in cast-iron cylinders, set in the furnace either vertically or horizontally, and provided with a tightly fitting lid at one end. The best plan consists in enclosing the wood to be charred in a second lighter case; this can be easily introduced into and withdrawn from the fixed cylinder, which is set in masonry, and protected from the direct action of the flame by a casing of fire-brick. From this kind of iron retort proceeds a tube connected with a condensing apparatus, where the liquid products of the decomposition may be arrested, whilst the uncondensable gases pass on, and are directed into the fire-place, in which they are consumed. After the heat has been continued for four or five hours, the end of the outer cylinder is removed, the inner case with its charge is withdrawn, and the whole, whilst still red

hot, plunged into an extinguisher or iron case, provided with a tightly fitting lid, which protects it from the action of the air; in this condition it is left to cool gradually.

In countries where wood is abundant, the charcoal is manufactured by a much ruder method. A plot of ground is levelled in or near the forest, a stake is driven into the ground, and a quantity of brushwood having been placed around its base, logs of wood are piled up regularly round the stake so as to form a mound, which is partially covered up with powdered charcoal, leaves, turf, and earth; the heap is then fired by introducing lighted fagots into an aperture left at the base of the mound for this purpose: large quantities of moisture are presently exhaled, and when the whole mass is thoroughly ignited, it is still more closely covered up from the air, the workmen regulating the admission of air as circumstances require; it is then allowed to burn out. When quite cold, the earth employed to stifle the combustion is removed, and the charcoal is fit for use. The combustion of one part of the wood is thus employed as a source of heat for charring the rest. Charcoal prepared in this manner is, for the purposes of fuel, preferable to that made in cylinders; it is denser and is more completely deprived of volatile matters, because the heat to which it is exposed is much more intense, and is continued for a much longer period. If the diameter of the heap be 10 metres or more, the operation is not complete in less than a month. A slow combustion is found to yield more charcoal than one which is rapidly effected. The resulting charcoal retains the form of the wood, but it is much reduced in size, generally not amounting to more than three-fourths of the bulk of the wood, and never exceeding one-fourth of its weight.

Experience shows it to be much more economical to employ dry wood in the preparation of charcoal, than wood in its green condition. Karsten found that 100 parts of recently felled wood, by drying at  $212^{\circ}$ , lost 57 parts; by raising the temperature to  $302^{\circ}$  ( $150^{\circ}$  C.), the loss upon the original weight amounted to not less than 67 parts; and the 33 parts of dry residue when charred left 25 parts of charcoal; but 100 parts of the same wood, if charred without any preliminary drying, left only 14 parts of charcoal. This remarkable difference in produce depends upon the decomposing action of charcoal at a high temperature upon water, in consequence of which much of the carbon escapes in the gaseous state in the form of carbonic oxide, whilst the hydrogen of the water also passes off as gas.

The object of preparing charcoal as a fuel is to get rid of mois-

ture and volatile matters, which, at the moment of their formation, greatly reduce the temperature of the burning mass, owing to the large quantity of heat which they carry off in the latent state. Charcoal also contains in the same bulk a larger amount of carbon than the wood which furnished it, and by supplying a more compact fuel concentrates into a smaller space the heat which it emits, a condition which, in metallurgical operations demanding a high temperature, is often of the greatest importance.

In the economy of material to be used as a combustible it is not sufficient to consider simply the absolute amount of heat which a given weight of the fuel emits whilst burning. The radiating power of a solid mass of fuel is much higher than that of a gaseous combustible, but the temperature of flame is very high. A fuel which burns with flame is therefore necessary where it is needful to communicate an elevated temperature to objects at a distance from the fire-grate, or to raise large masses to a uniform temperature. Wood and bituminous coals are, consequently, particularly useful in the glass furnace and in the porcelain kiln; whilst in heating boilers, and objects in which direct radiation can act with its full effect, coke, anthracite, and coal which burns with but little flame, are especially valuable. In an ordinary open fire, these flameless coals are also the most useful, as the heat is thrown off by them into the room most completely, instead of being carried up the chimney with the gaseous products.

Charcoal never consists solely of pure carbon. According to the experiments of Violette, 100 parts of black alder (*bourdaine*) wood, charred at the following temperatures, gave amounts of charcoal progressively diminishing; but the per-centage of carbon in the residual charcoal was found to increase, as shown in the table.

Temperature of charring.		Per-centage of charcoal.	Per-centage of carbon in charcoal.
°C.	°F.		
250	482	50	65
300	572	33	73
400	752	20	80
1500	2732	15	96

A peculiar kind of charcoal, but imperfectly burned, and of a reddish-brown colour, termed by the French *charbon roux*, is occasionally prepared for the manufacture of the gunpowder used for sporting purposes. Powder made with this charcoal absorbs moisture more rapidly than ordinary gunpowder. *Charbon roux* is procured by forcing steam, under a pressure of about two atmospheres, through a coil of heated pipe, and directing this super-heated steam, at about



536° (280° C.), into the iron cylinder containing the wood: in a few hours the charring of the wood is effected. The following is stated by Regnault to be its average composition in 100 parts :—

Carbon	...	...	...	...	71.42
Hydrogen	...	...	...	...	4.85
Oxygen and Nitrogen	...	...	...	...	22.91
Ash	...	...	...	...	0.82

*Animal Charcoal*, or ivory black, is prepared by heating bones in cylinders in a manner similar to that employed for wood charcoal.

(355) *General Properties of Carbon*.—Carbon in all the forms above mentioned is chemically the same. At atmospheric temperatures it is one of those substances in which chemical attraction exhibits least activity; consequently a superficial charring is frequently resorted to with a view to protect wood from decay, as in the case of piles which are driven into mud or into the beds of rivers, to serve as foundations. For the same reason it is a common practice to char the interior of tubs and casks destined to hold liquids. Lampblack furnishes the most indestructible of black pigments, and has long been employed on this account as the basis of printing ink. The diamond is a non-conductor of electricity; in its other forms carbon is an excellent conductor, ranking next to the metals in this respect. In a state of fine subdivision it is a bad conductor of heat, but its conducting power increases with its density. Finely divided charcoal is usually stated to have strong antiseptic powers. It certainly has a remarkable action upon putrescible substances; but Stenhouse has shown that this action consists in a rapid process of oxidation dependent upon the power which charcoal, when in a finely divided state, possesses of condensing oxygen. The offensive effluvia from animal matter in an advanced stage of putrefaction disappear when the putrefying substance is covered with a layer of charcoal; it continues to decay, but without emitting any odour, till at length all the carbon is dissipated as carbonic anhydride, the hydrogen as water, and the nitrogen remains as a nitrate. The remarkable power possessed by charcoal of absorbing various bodies, particularly colouring matters and many bitter principles, when in a finely divided state (54), as well as its property of condensing a large proportion of gaseous matters within its pores (65), has been already mentioned. So rapid is this action, that Stenhouse has proposed to use a respirator filled with charcoal, to protect the mouth and nostrils in an infected atmosphere; and the employment of trays of powdered wood charcoal in dissecting-rooms, in the wards of hospitals, and in situations where putrescent

animal matter is present, is found to exert a most beneficial influence in sweetening the atmosphere by absorbing and decomposing the offensive gases. These properties render charcoal a valuable material in the construction of filters, not only for decolorizing purposes, but likewise for assisting in purifying water for domestic use. It is now also employed successfully to prevent the escape of noxious vapours at the ventilating openings of the sewers, as it allows the free passage of air, but condenses the offensive effluvia in its pores, where they are destroyed by a process of oxidation. It will continue active for years if kept dry.

Carbon is usually regarded as neither fusible nor volatile; but in the course of some experiments with a voltaic battery of intense energy, consisting of 600 cells of Bunsen's construction, connected so as to form a battery of 100 pairs of 6 cells each, Despretz found on operating upon carbon points in an exhausted receiver, that the vessel became filled with a dark cloud, which was deposited upon the sides of the glass as a black crystalline powder; and by exposing charcoal obtained from pure sugar, or from essence of turpentine, to the action of the battery in a small crucible of pure charcoal connected with the positive electrode, the whole of the charcoal powder became cemented into a coherent mass which appeared to have been fused, and which exhibited the properties of graphite.

At high temperatures carbon combines rapidly with oxygen, and will remove it from a great number of its compounds, especially from the oxides of the metals; hence the various forms of carbon are very extensively employed in the reduction of these substances to the metallic condition. The deoxidizing power of carbon is sometimes exerted at the ordinary temperature of the air. Schönbein found that ferric salts may be reduced to the condition of ferrous salts, by simply agitating their solutions with charcoal powder, and the mercuric are, in like manner, converted into mercurous salts. Charcoal decomposes steam at a red heat; hydrogen is liberated, and a mixture of carbonic oxide and carbonic anhydride is formed.

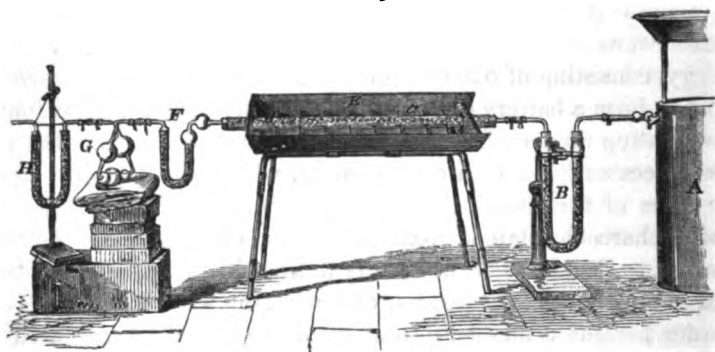
It was long supposed that sulphur is the only non-metallic element besides oxygen with which carbon can be made to unite directly, and a high temperature is required in this case also to effect the combination. The experiments of Berthelot have proved that by igniting charcoal intensely by means of the voltaic arc in a current of pure hydrogen, a particular hydrocarbon, acetylene,  $C_2H_2$ , is formed.

The compounds of carbon with the metals are termed *carburets* or *carbides*.

(356) *Synthesis of Carbonic Anhydride*.—Since a knowledge of the composition of carbonic anhydride is a fundamental datum for the analysis of organic compounds, the proportion in which oxygen combines with carbon to produce carbonic anhydride has been determined with the greatest care, by the combustion of weighed quantities of diamond, of graphite, and of charcoal, in a stream of dry oxygen.

The apparatus employed for this purpose is indicated in fig. 298. A represents a gas-holder filled with oxygen; B a tube containing fragments of

FIG. 298.



caustic potash, or pumice-stone moistened with sulphuric acid, for removing all traces of moisture from the oxygen; *c d* is a tube of hard glass traversing the sheet-iron furnace, E. At *c* is a platinum tray containing the weighed portion of diamond or graphite; the front of the tube, *d*, is occupied by a column of cupric oxide, the object of which is to oxidize completely any trace of carbonic oxide which might be formed. The apparatus is filled with dry oxygen by opening the stopcock of the gas-holder, A, to a regulated distance, and the fore-part of the tube, *d*, is brought to a red heat by means of heated charcoal; the heat is then applied to the spot, *c*, where the carbon lies. The carbon burns and becomes converted into carbonic anhydride, which traverses the column of heated cupric oxide; F is a weighed tube, filled with calcic chloride, which, if water were present, would be found to increase in weight, but in which no deposit of moisture is formed if the experiment be properly conducted. The carbonic anhydride passes on, and is absorbed by a strong solution of potash contained in the bulbs of the Liebig's apparatus, shown at G. The excess of oxygen absorbs moisture as it passes through this liquid, but before it is allowed to escape into the air it is rendered perfectly dry by causing it to pass through an additional tube, H, filled with fragments of caustic potash. The increase in weight acquired by the tubes G and H furnishes the weight of the carbonic anhydride corresponding to the quantity of carbon consumed, and the quantity of carbon burned is ascertained by weighing the platinum tray and its contents after the experiment has terminated.

By experiments conducted upon this principle it has been determined that 12 parts of carbon require for conversion into carbonic anhydride exactly 32 parts of oxygen (Dumas and Stas; *Ann. de Chimie*, III. i. 5).

Diamond, graphite, and charcoal are thus shown to be chemically the same substance, though they differ entirely in properties; these three conditions being allotropic modifications of carbon (87), the differences in properties arising not from differences in their chemical nature, but in their molecular arrangement.

If a piece of pure carbon be burned in a jar of oxygen over mercury, it will be found after the combustion is over, and the gas has cooled to the initial temperature of the oxygen, that its volume has undergone no permanent change: the bulk of the oxygen, therefore, is not altered by this combination; the carbonic anhydride which is formed occupies precisely the same space as the oxygen which has entered into its composition.

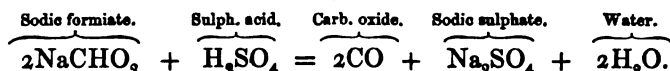
(357) CARBONIC OXIDE: ( $\text{CO}=28$ ); *Sp. Gr.* 0.967; *Atomic and Mol. Vol.*    *Rel. wt.* 14.—It has been stated that carbonic anhydride is wholly deprived of its oxygen when heated with potassium; but if some metal, such as zinc or iron, which has a less powerful attraction for oxygen, be substituted for the potassium, the carbonic anhydride will only be partially deoxidized; the metal will deprive it of exactly half the oxygen which it contains, and a new gaseous body, termed *carbonic oxide*, will be produced. The bulk of this new gas is exactly equal to that of the carbonic anhydride that furnished it. Carbonic oxide, mixed with free hydrogen, is also obtained abundantly when steam is transmitted over charcoal heated to bright redness;  $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$ .

*Preparation.*—1. Carbonic oxide may be conveniently prepared by mixing powdered chalk with an equal weight of iron or zinc filings, and exposing the mixture to a red heat in a gun-barrel. The chalk when ignited gives off carbonic anhydride, which in contact with the heated metal is decomposed; oxide of iron or of zinc is formed, quick-lime remains in the retort mixed with the metallic oxide, and the carbonic oxide gas after being washed with water containing slaked lime in suspension, with a view to absorb any undecomposed carbonic anhydride, may be collected over water, in which it is but slightly soluble. These chemical changes may be represented in the following manner when zinc is used;  $\text{CaCO}_3 + \text{Zn} = \text{CaO} + \text{ZnO} + \text{CO}$ .

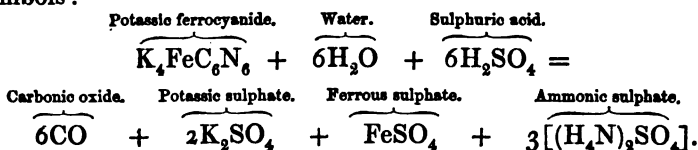
2.—Carbonic oxide is often produced abundantly in the ordinary process of combustion in stoves and furnaces: this mode of its formation is important, for it exercises a material influence upon the economy of combustion, inasmuch as all the carbonic oxide thus carried off unburnt represents so much fuel wasted; while in many metallurgic operations the carbonic oxide so pro-

duced plays a conspicuous part in the reduction of the ore to the metallic state, the oxides of iron, lead, copper and many other metals, being reduced when heated with it, whilst carbonic anhydride is formed. It is owing to the production of carbonic oxide that anthracite can be employed in roasting the copper ores at Swansea, flame being essential to the due performance of the process (869). The formation of carbonic oxide in an open fire which is burning steadily without emitting smoke is often evidenced by the flickering blue flame seen playing over the glowing embers. In this case carbonic anhydride is first formed at the bottom of the grate, from the free access of air to this part of the burning fuel; but the carbonic anhydride as it traverses the red-hot coke enters into combination with an additional quantity of carbon, and the anhydride losing half its oxygen, is converted into its own bulk of carbonic oxide: at the same time the carbon of the heated fuel which has entered into combination with this removed oxygen furnishes another equal quantity of the same gas: the heated carbonic oxide takes fire as soon as it mixes with the air which passes over the upper surface of the fire. The reaction between the hot carbon and carbonic anhydride may be thus represented:  $\text{CO}_2 + \text{C} = 2\text{CO}$ .

3.—If one of the formiates be treated with oil of vitriol, pure carbonic oxide is obtained; for instance:—

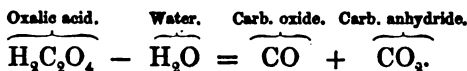


4.—Carbonic oxide may also be formed in several other ways. Half an ounce (15 grms.) of the yellow prussiate of potash, if heated in a retort with 4 or 5 ounces (140 grms.) of oil of vitriol, yields more than a gallon (4 or 5 litres) of the pure gas (Fownes). Care is requisite in applying the heat, because when the temperature rises to a certain point the extrication of the gas takes place with tumultuous rapidity. The reaction is in this case of a complicated nature, but is expressed by the annexed symbols:—



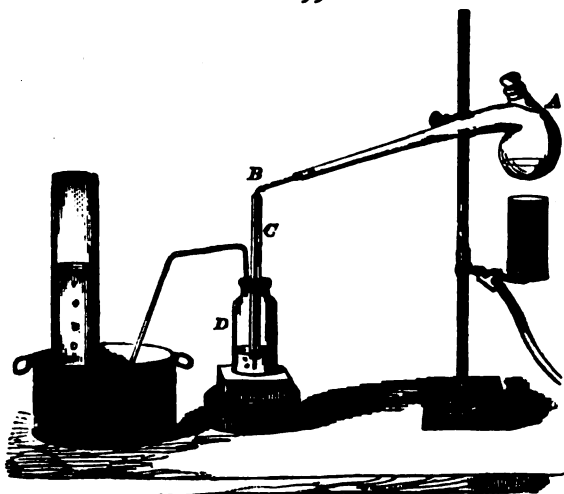
5.—Another method by which carbonic oxide may be obtained with facility consists in heating oxalic acid with 5 or 6 times its weight of oil of vitriol. The oxalic acid is thus deprived of the elements of water, and is resolved into a gaseous

mixture consisting of equal measures of carbonic anhydride and carbonic oxide: by allowing the mixed gases to pass through a vessel filled with a solution of potash, or with milk of lime, the carbonic anhydride is absorbed, and the carbonic oxide may be collected in a state of purity. The decomposition may be thus explained:—



A convenient mode of washing the gas is shown at B, fig. 299: the bent tube is connected to the neck of the retort, A, and passes to the bottom of a wider tube, C, open both at top and bottom, which passes into the washing bottle, D: a moveable gas-tight joint, which can be mounted or dismounted in a moment, is thus obtained.

FIG. 299.



*Properties.*—Carbonic oxide is a transparent colourless gas, with a faint oppressive odour. It is much lighter than carbonic anhydride, having a specific gravity of 0.967 (Wrede.) All attempts at its liquefaction have as yet been unsuccessful. It is but very sparingly soluble in water, 100 volumes of this liquid dissolving 3.28 volumes at 32°, and 2.43 at 59° (15° C.) (Bunsen). When respired, even though largely diluted with air, it acts as a direct poison, producing a peculiar sensation of oppression and tightness of the head. It does not support combustion, but burns itself with a beautiful pale blue light, producing by its combination with oxygen carbonic anhydride only. A solution of cupreous chloride in hydrochloric acid, or of a cupreous salt

dissolved in ammonia, gradually absorbs carbonic oxide if agitated with it. The solution of this compound is not decomposed by dilution, but if the liquid be boiled most of the gas is expelled unaltered. The compound with cupreous chloride crystallizes in fatty looking scales, consisting of  $(\text{CO}, \text{CuCl}, \text{H}_2\text{O})$ , but by exposure to air it is quickly decomposed. Carbonic oxide is absorbed by potassium if the metal be heated to about  $176^\circ$  ( $80^\circ \text{C.}$ ) in the gas, and according to Brodie, the combination occurs in the proportion shown by the formula,  $\text{COK}$ . This property is sometimes employed for separating carbonic oxide from its mixture with other inflammable gases in the process of analysing mixtures of such gases.

Carbonic oxide has been supposed to form the radicle of a numerous series of compounds; it even enters directly into combination with potassic hydrate when heated with it, converting it into potassic formiate:  $\text{KHO} + \text{CO} = \text{KCHO}_2$  (Berthelot).

*Composition.*—The chemical composition of carbonic oxide may be ascertained in the following manner:—Introduce into the bent eudiometer (fig. 290) a certain quantity, say 20 measures, of carbonic oxide, then add 20 measures of pure oxygen; pass the electric spark with the precautions already described: the 40 measures of gas will become diminished to 30 measures. If a little solution of potash be introduced, 20 measures of the residual gas will disappear, leaving 10 measures of unaltered oxygen: the 20 measures of gas absorbed are carbonic anhydride. Now carbonic anhydride contains its own bulk of oxygen, but the 20 measures of carbonic oxide have required only 10 measures, or half their bulk, of oxygen to convert them into the anhydride. Carbonic oxide therefore must have contained the other 10 measures of oxygen; in other words, half its bulk of oxygen. But the specific gravity of carbonic oxide is 0.9674; deduct from this

$$0.5528 = \text{half the specific gravity of oxygen}$$

0.4146; this remainder is the weight of the carbon combined with 0.5528 of oxygen.

Now  $0.5528 : 0.4146 :: 16 : 12$ . The proportion by weight of oxygen to carbon in carbonic oxide is therefore as 16 to 12, or 1 atom of each, and its composition may be thus represented:—

		By weight.	By volume.	Sp. gr.
Carbon	C = 12	or 42.86	2? or 1.0?	= 0.4146
Oxygen	O = 16	57.14	1	0.5 = 0.5528
Carb. oxide	CO = 28	100.00	2	1.0
				0.9674

Carbonic oxide and carbonic anhydride, widely as they differ in properties, consist, it is evident, of the same elements; but the proportions of the two elements differ in the two cases. Carbonic oxide is the compound of carbon that contains the smallest proportion of oxygen, the relative composition of the two bodies being :

		C.	O.	Carbon.	Oxygen.
Carbonic oxide	CO =	28 or 12	+ 16	= 42·86	+ 57·14
Carbonic anhydride	CO <sub>2</sub> =	44	12 + 32	= 27·28	+ 72·72
In 100 parts.					

## CHAPTER V.

### COMPOUNDS OF NITROGEN WITH OXYGEN AND WITH HYDROGEN.

#### § I. COMPOUNDS OF NITROGEN WITH OXYGEN.

(358) THE attraction of nitrogen for oxygen is much feebler than that of either carbon or hydrogen for oxygen, so that it is not easy to procure their direct union,—especially as the temperature emitted by the nitrogen and oxygen in the act of combination is comparatively low. Nitrogen, notwithstanding, forms with oxygen five distinct compounds, containing, respectively, 1, 2, 3, 4, and 5 atoms of oxygen with 2 atoms of nitrogen. They may all be obtained free from water.

These compounds have been named

		By weight.		In 100 parts.		Mol. Vol.
		N.	O.	Nitrogen.	Oxygen.	
Nitrous oxide	N <sub>2</sub> O =	44 or 28	+ 16	63·64	+ 36·36	<input type="text"/>
Nitric oxide	NO =	30	14 + 16	46·67	+ 53·33	<input type="text"/>
Nitrous anhydride	N <sub>2</sub> O <sub>3</sub> =	76	28 + 48	36·85	+ 63·15	<input type="text"/>
Peroxide of nitrogen	N <sub>2</sub> O <sub>4</sub> =	92	28 + 64	30·44	+ 69·56	<input type="text"/>
Nitric anhydride	N <sub>2</sub> O <sub>5</sub> =	108	28 + 80	25·93	+ 74·07	<input type="text"/>

(359) NITRIC ACID; *Hydric Nitrate*, HNO<sub>3</sub> = 63; *Sp. Gr. of Liquid at 59° (15° C.)* 1·517; *Boiling-pt.* 184° (84°·5 C.).—The most important of the compounds of oxygen with nitrogen is that which when in combination with water was formerly called *aqua fortis*, and is now designated nitric acid. It was known to the alchemists, but its true composition was first determined by Cavendish in 1785. When nitrogen is mixed with 12 or 14 times its bulk of hydrogen, and a jet of the mixed gas is allowed to burn in air or in oxygen, the water which is formed has a sour taste and an acid reaction, owing to the simultaneous formation of a small quantity of nitric acid. In this case the nitrogen burns by the aid of the heat developed during the combustion of the hydrogen, and the oxidized compound combines at once with the water



formed, which much increases its chemical stability. It was, indeed, owing to the accidental production of nitric acid in the course of his experiments on the formation of water by the combustion of hydrogen, that Cavendish was induced to institute the train of researches which terminated in this important discovery.

If 2 volumes of nitrogen be mixed with 5 volumes of oxygen, and introduced into the bent eudiometer (fig. 290) and the tube be filled up with an infusion of blue litmus in distilled water, a series of electric sparks may be transmitted through the mixture by means of a Ruhmkorff's coil: under these circumstances the two gases will combine slowly, and the litmus will be reddened. The heat of the spark determines the combination of the gases just at the spot through which it passes, but the action does not extend further. In like manner, if a number of sparks be passed from the electrical machine, between two metallic points, over moistened litmus-paper, in air, a red spot will be produced upon the paper, owing to the formation of nitric acid in minute quantity by the combination of oxygen with nitrogen in presence of aqueous vapour in the air. During stormy weather, and indeed whenever a flash of lightning passes through a moist atmosphere, the same compound is produced in appreciable quantity. Indeed, it is rare to meet with rain water in which traces of ammoniacal nitrate may not be detected, if the experiment is made with accuracy. Ammonia likewise yields nitric acid under certain circumstances by slow oxidation (369).

Nitrates of potassium and sodium also occur in the form of an efflorescence on the soil, especially in tropical climates, as in some parts of India and Peru. The compound formed with potassium constitutes the nitre or saltpetre of commerce. The nitrates of the alkali-metals are often present in the water of wells in towns or in the vicinity of cemeteries, the nitric acid being in these cases produced by the oxidation of azotised animal matters, as they undergo decomposition during the percolation of their aqueous solution through the soil.

*Preparation.*—It is from one of the nitrates that the acid is always obtained for chemical purposes. When potassic nitrate is heated with a powerful acid, such as the sulphuric ( $\text{H}_2\text{SO}_4$ , dihydric sulphate) a true double decomposition occurs. The potassium and hydrogen change places, forming on the one hand dipotassic sulphate ( $\text{K}_2\text{SO}_4$ ), and on the other hydric nitrate, or nitric acid ( $\text{HNO}_3$ ). The dipotassic sulphate remains in the retort, whilst the more volatile nitric acid distils over, and may be condensed in the usual manner. The method of procuring nitric acid offers a good

example of the general principle upon which acids which admit of being distilled without experiencing decomposition are obtained from their metallic salts; the ordinary acids, it must be remembered, are *salts of hydrogen*. In preparing nitric acid on the small scale, equal weights of nitre and oil of vitriol are placed in a glass retort, and the distillation is proceeded with in the manner shown in figs. 143 and 144, Part I. p. 346.

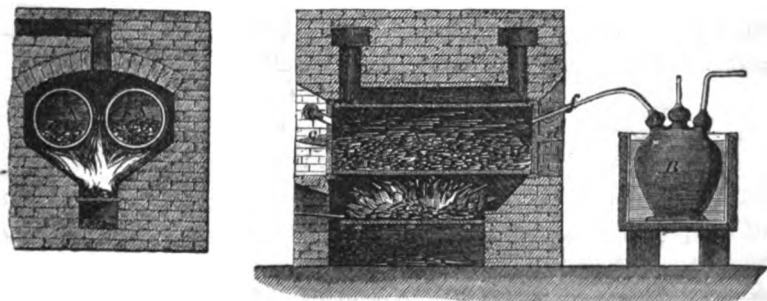
During the distillation red fumes appear in the retort, arising from a partial decomposition of the acid, and the formation of some of the lower oxides of nitrogen, whilst a yellowish corrosive liquid is condensed in the receiver: this liquid is hydric nitrate, or concentrated nitric acid ( $\text{HNO}_3$ ); it fumes strongly in the air, and emits a powerfully irritating and acid odour.

On the large scale, iron retorts, fig. 300, coated with fire-clay on the inside of the upper part, where they are exposed to the acid vapours, are employed for

1.

FIG. 300.

2.



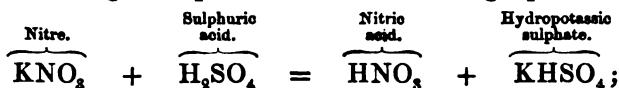
the distillation, and sodic nitrate is substituted for potassic nitrate, as it is a cheaper salt, and likewise yields 9 per cent. more nitric acid than potassic nitrate. The cylinders or retorts are arranged in pairs in a furnace, so that each fire heats two cylinders, as shown in the section, 1. The cylinders are supplied with a moveable lid, *c, d*, at each end. The nitrate is introduced into the retort, *a*, through the opening at *c*, which is closed during the distillation by a stone lid, fitted accurately to the aperture; and the oil of vitriol is added by a funnel at *e*, after the retort is closed. As soon as the acid is introduced, the funnel is withdrawn, and the opening at *e* is closed with a plug. The nitric acid as it distils over passes through the pipe *f*, and is condensed in a series of stoneware bottles, the first of which is seen at *b*. The acid collected in the first receiver is always contaminated with sulphuric acid, and that in the last is rather dilute, as water is placed in it to condense the nitrous fumes.

Upon the large scale it is customary to employ a proportion of sulphuric acid smaller than that used when the distillation is performed in glass vessels, for it is quite possible to effect a complete decomposition of the nitrate by heating it with one-half its weight of oil of vitriol. Under these circumstances, however, a higher temperature is needed to expel the last portions of acid, and

a considerable quantity of the nitric acid is thereby decomposed and wasted. The residue in the retort, when the smaller quantity of sulphuric acid is used, is much less soluble in water, and consequently is much more difficult of removal: but in the iron cylinder of the manufacturer this is of no moment, because the saline mass can easily be detached by the use of iron tools when the distillation is at an end.

The cause of these differences in the result of the processes adopted on the large and on the small scale lies in the fact that sulphuric acid by its reaction upon potash gives rise to two different sulphates, one of which contains twice as much potassium as the other; the acid sulphate consisting of  $\text{KHSO}_4$ , being a hydro-potassic sulphate, while the common neutral sulphate, or dipotassic sulphate contains  $\text{K}_2\text{SO}_4$ .

When nitre and sulphuric acid are mixed in the proportion of equal weights (or 1 equivalent of nitre, and 2 of acid), the hydro-potassic sulphate is obtained, and nitric acid distils readily; half the hydrogen only of the sulphuric acid being displaced by potassium: the change is represented in the following equation:—



but if the nitrate be mixed with sulphuric acid in the proportion of 2 equivalents of each, the decomposition takes place in two successive stages; in the first of these, half the nitre only is decomposed, hydro-potassic sulphate being furnished in the first instance as before, and a gentle heat only is needed for the distillation of the nitric acid so produced. The following equation may be employed to represent this first stage of the change:—



But as soon as the first half of the nitric acid has passed over, the temperature begins to rise, and the hydro-potassic or acid sulphate reacts on the undecomposed nitre; the second half of the nitric acid is then formed, but at the same time is partially decomposed, particularly towards the end of the operation: finally, the whole of the potassium remains in the retort in the form of the sparingly soluble neutral or dipotassic sulphate. This second stage of the decomposition is exhibited in the subjoined equation:



Similar equations would represent the reactions with sodic nitrate, substituting the symbol Na for K, wherever the latter occurs.

*Nitric acid* (the so-called monohydrate),  $\text{HNO}_3$ ; *Sp. gr. of liquid*, 1.517, at  $15^\circ \text{C.}$ ; *Boiling-pt.*  $184^\circ$  ( $84^\circ.5 \text{C.}$ ); *Comp. in 100 parts*,  $\text{N}_2\text{O}_5$ , 85.72;  $\text{H}_2\text{O}$ , 14.28.—The acid which is obtained by the foregoing process is of a yellowish or red colour, owing to the presence of some of the lower oxides of nitrogen; these may, if necessary, be got rid of by mixing the acid with an equal bulk of oil of vitriol, and submitting the mixture to distillation. If the first portions be collected, and gently warmed while a current of dry air is sent through the acid, sheltered from strong daylight, a pure acid remains behind as colourless as water, and quite free from the lower oxides of nitrogen. It is, however, so unstable in this concentrated form that it cannot be redistilled alone without experiencing partial decomposition. When exposed to the sun's light a similar decomposition is produced; oxygen gas is evolved, and the acid becomes coloured owing to the formation of lower oxides of nitrogen. When pure, nitric acid is a colourless, limpid, fuming, powerfully corrosive liquid, which freezes at about  $-40^\circ$ . It begins to boil at  $184^\circ$ , but the temperature rises gradually, owing to the decomposition of the liquid; oxygen and nitrous fumes are evolved; the boiling-point continues to rise slowly till it reaches  $250^\circ$  ( $121^\circ \text{C.}$ ), at which point the acid in the retort has a composition approaching to  $(2\text{HNO}_3, 3\text{H}_2\text{O})$ , and distils unchanged.

Owing to the facility with which the acid parts with oxygen, it is continually employed as an oxidizing agent. If it be dropped into hot finely powdered charcoal, the charcoal burns vividly; if it be mixed with a little oil of vitriol, and poured into oil of turpentine, the mixture bursts into flame. Sulphur, phosphorus, and iodine are oxidized by it, the phosphorus almost with explosive violence. Nitric acid is one of the most corrosive substances known. It destroys all animal textures rapidly, and if slightly diluted stains the skin, wool, feathers, and all albuminous bodies of a bright yellow colour. The acid in a somewhat diluted state is, indeed, often used to impart a permanent yellow dye to woollen and silken goods. Nitric acid acts violently upon tin or iron filings, especially if they be previously moistened with a few drops of water; and indeed it attacks most of the metals except gold, platinum, rhodium, and iridium. The action of nitric acid upon the metals varies with its temperature and degree of dilution: but its energy is most manifest when diluted to a specific gravity of from 1.35 to 1.25. The pure concentrated acid,  $\text{HNO}_3$ , is in

fact without action upon tin, iron, bismuth, and many other metals at ordinary temperatures. The presence of nitrous acid in the nitric acid greatly increases its oxidizing power, for owing to the instability of nitrous acid this compound parts with its oxygen very readily. At a temperature of  $0^{\circ}$  ( $-18^{\circ}$  C.) the acid, whether concentrated or dilute, is without action on copper, but it dissolves zinc rapidly.

(360) *Action of Acids on Metals.*—The chemical action of nitric acid upon the metals is a process of considerable importance, but in order to study with advantage the effects to which it gives rise it will be useful to consider the action of acids upon the metals from a general point of view. It has already been stated that the metals unite directly with many of the non-metallic elements, such as chlorine, oxygen, and sulphur. Antimony, for example, will take fire spontaneously if allowed to fall in fine powder into chlorine. Iron will burn in oxygen if first heated to the point of ignition; and copper turnings, if mixed with powdered sulphur, will, on the application of heat, combine with the sulphur, and during the action will emit a vivid light. The metallic oxides, when presented to the acids, become quickly dissolved; cupric oxide is brought into solution by diluted sulphuric acid, zincic oxide quickly disappears when agitated with hydrochloric acid, and plumbic oxide is rapidly dissolved by acetic acid.

But a metal will not unite directly with an anhydride. Union between a metallic oxide and an anhydride may, however, occur, though, even then, the action is much favoured by the presence of water. Sulphuric anhydride, for instance, does not act upon iron, but the anhydride is immediately absorbed by caustic potash,  $\text{KHO} + \text{SO}_3$  becoming  $\text{KHSO}_4$ ; and in like manner, carbonic anhydride is rapidly absorbed by slaked lime.

When the metals are presented to the acids other phenomena are observed; a brisk action frequently takes place, accompanied by the evolution of a gas, and it is very often stated that the metal first becomes oxidized, and is then dissolved by the acid.

It is not, however, necessary to assume that the metal always undergoes oxidation as a preliminary step, for it may be supposed that in many cases the metal simply displaces the hydrogen of the acid. When, for example, zinc is placed in diluted sulphuric acid, the metal is dissolved with rapidity, whilst hydrogen escapes in the gaseous form;  $\text{H}_2\text{SO}_4 + \text{Zn}$  yielding  $\text{ZnSO}_4 + \text{H}_2$ . A similar result is obtained when iron or tin is dissolved in hydrochloric acid, ferrous or stannous chloride being produced, whilst hydrogen is given off, the reaction in the case of iron being re-

presented by the equation,  $2\text{HCl} + \text{Fe} = \text{FeCl}_2 + \text{H}_2$ . When an oxide is employed instead of a metal, the hydrogen, instead of escaping as gas, is eliminated in the form of water; for instance, in the action of zincic oxide upon sulphuric acid, the change may be represented as  $\text{ZnO} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2\text{O}$ ; and again with cupric oxide and hydrochloric acid,  $\text{CuO} + 2\text{HCl} = \text{CuCl}_2 + \text{H}_2\text{O}$ .

The ordinary action of metals upon sulphuric acid, in which the components of the acid are united by powerful chemical ties, is, as we have just seen, comparatively simple; but where the elements of the acid are but feebly held together, as is the case with nitric acid, the actions are often more complicated. When, for example, silver or copper is dissolved in nitric acid, hydrogen may as before be displaced from the acid by the metal which becomes dissolved; but owing to the facility with which nitric acid parts with its oxygen no hydrogen is set free—for at the moment of its liberation it becomes oxidized at the expense of the elements of the nitric acid—one of the lower oxides of the nitrogen is formed, and occasions the disengagement of ruddy fumes instead of the colourless and inflammable hydrogen. In many instances it is probable that the radicle of the acid itself is deoxidized by the direct action of the metal, the oxide of the metal then forming a salt with the undecomposed portion of acid by double decomposition, as already explained where an oxide acts upon an acid:—for example, when metallic silver acts upon heated nitric acid, a portion of the acid furnishes oxygen, disengaging nitric oxide, whilst the freshly formed oxide of silver reacts upon another portion of the acid;  $3\text{Ag}_2 + 2\text{HNO}_3$ , first becoming  $3\text{Ag}_2\text{O} + 2\text{NO} + \text{H}_2\text{O}$ , and then  $\text{Ag}_2\text{O} + 2\text{HNO}_3$  yields  $\text{H}_2\text{O} + 2\text{AgNO}_3$ . The exact nature of the decomposition, however, varies in different cases; silver when allowed to become dissolved slowly in the cold in an excess of diluted nitric acid produces nitrous acid ( $\text{HNO}_2$ ), which remains in solution;  $\text{Ag}_2 + 3\text{HNO}_3$  giving  $2\text{AgNO}_3 + \text{H}_2\text{O} + \text{HNO}_2$ , and the metal is dissolved without evolution of gas: a similar effect is also produced by palladium. With metals which attack the acid more vigorously, such as copper or mercury, nitric acid of moderate concentration (sp. gr. 1.25 to 1.3) disengages nitric oxide in large quantity: for example,  $3\text{Cu} + 8\text{HNO}_3$  yields  $2\text{NO} + 3(\text{Cu}_2\text{NO}_3) + 4\text{H}_2\text{O}$ ; but if the acid be more highly concentrated (sp. gr. 1.42), peroxide of nitrogen is disengaged abundantly;  $\text{Cu} + 4\text{HNO}_3$  yielding  $\text{Cu}_2\text{NO}_3 + 2\text{NO}_2 + 2\text{H}_2\text{O}$ . And when the decomposition occurs at a high temperature, free nitrogen is usually disengaged in considerable quantity, the acid undergoing

complete deoxidation;  $5\text{Cu} + 12\text{HNO}_3 = 5(\text{Cu}_2\text{NO}_3) + \text{N}_2 + 6\text{H}_2\text{O}$ . If the metal, like zinc, has a still more energetic action, the acid when dilute yields nitrous oxide amongst its gaseous products;  $4\text{Zn} + 10\text{HNO}_3 = \text{N}_2\text{O} + 4(\text{Zn}_2\text{NO}_3) + 5\text{H}_2\text{O}$ . When zinc or tin is used with a stronger acid, ammonia is amongst the products; for instance,  $4\text{Zn} + 9\text{HNO}_3 = 4(\text{Zn}_2\text{NO}_3) + 3\text{H}_2\text{O} + \text{H}_3\text{N}$ , the ammonia combining with the excess of acid employed.

(361) *Hydrates of Nitric acid*.—When concentrated nitric acid is exposed to the air it absorbs moisture, and if 70 parts of the concentrated acid be mixed with 30 of water it emits a sensible amount of heat. Under these circumstances a hydrate of nitric acid of considerable stability appears to be formed with a composition represented by the formula  $(2\text{HNO}_3, 3\text{H}_2\text{O})$ . This hydrate would contain 60 per cent. of the anhydride  $\text{N}_2\text{O}_5$  and 40 of water: such an acid has a sp. gr. of 1.424; it boils at  $250^\circ$  ( $121^\circ$  C.), and may be distilled, under ordinary pressures apparently unaltered. A weaker acid when heated parts with its water till it arrives at this density, and a stronger acid, when distilled, also loses acid until reduced to this point, the liquid in the retort eventually, in both cases, acquiring a density of 1.424. This hydrate nevertheless is not perfectly stable when distilled, for by conducting the distillation at reduced pressures, Roscoe found that the density of the acid in the retort has no real fixed point, and that an acid may be obtained which does not correspond in composition to any definite hydrate, but that the proportion of water varies with the pressure under which the boiling takes place.

*Strength of Nitric Acid (Ure).*

Specific gravity.	$\text{N}_2\text{O}_5$ in 100 parts by weight.	Specific gravity.	$\text{N}_2\text{O}_5$ in 100 parts by weight.
1.5000	79.700	1.2887	39.053
1.4940	77.303	1.2705	36.662
1.4850	74.918	1.2523	34.271
1.4760	72.527	1.2341	31.880
1.4670	70.136	1.2148	29.489
1.4570	67.745	1.1958	27.098
1.4460	65.354	1.1770	24.707
1.4346	62.963	1.1587	22.316
1.4228	60.572	1.1403	19.925
1.4107	58.181	1.1227	17.534
1.3978	55.790	1.1051	15.143
1.3833	53.399	1.0878	12.752
1.3681	51.008	1.0708	10.361
1.3529	48.617	1.0540	7.970
1.3376	46.226	1.0375	5.579
1.3216	43.835	1.0212	3.188
1.3056	41.444	1.0053	0.797

The preceding table indicates the per-centage of nitric anhydride,  $N_2O_5$ , formerly called dry nitric acid, contained in aqueous solutions of nitric acid of various specific gravities.

(362) *Nitric Anhydride*, or *Dinitric Pentoxide* ( $N_2O_5$ ).—*Fusing pt.*  $85^\circ$  ( $29^\circ.5$  C.); *Boiling pt.*  $113^\circ$  ( $45^\circ$  C.).—This substance is a very unstable compound, which may be obtained in the form of perfectly transparent, brilliant, colourless crystals, derived from the right rhombic prism; they melt at  $85^\circ$  and boil at  $113^\circ$ : at about the temperature last-named the compound begins to undergo decomposition. Sometimes the crystals, even if kept in sealed tubes, become decomposed at the ordinary atmospheric temperature, and the tube bursts with a dangerous explosion from the pressure exerted by the liberated gases. The crystals are dissolved rapidly by water, emitting much heat, and producing ordinary hydrated nitric acid.

In order to procure the anhydride, a uniform current of perfectly dry chlorine gas is transmitted very slowly over crystals of well-dried argentic nitrate; the salt is at first heated to about  $203^\circ$  ( $95^\circ$  C.), till the decomposition has commenced, and the temperature is then lowered to about  $140^\circ$  ( $60^\circ$  C.). The operation is one of considerable delicacy, and requires attention to a number of minute precautions, for the details of which the reader is referred to Deville's paper (*Ann. de Chimie*, III. xxviii. 241.). The chlorine displaces the nitron ( $NO_2$ ) from the argentic nitrate; argentic chloride is formed, and nitron breaks up into nitric anhydride whilst oxygen escapes. By surrounding the receiver with a freezing mixture, the nitric anhydride is condensed in crystals. The decomposition may be represented in the following manner, though it is probably not quite so simple:—



Deville ascertained the composition of nitric anhydride by estimating the quantity of nitrogen which a given weight of the compound furnished after the oxygen had been removed from it by transmitting its vapours over finely divided metallic copper, which, at a high temperature, combines rapidly with the oxygen; 100 parts by weight of the anhydride were thus found to contain 25.9 of nitrogen; the deficiency, 74.1, is oxygen: or 28 parts of nitrogen are united with 80 of oxygen.

(363) *Common Impurities of the Acid*.—The nitric acid of commerce is liable to be contaminated with a variety of foreign matters, of which sulphuric acid, chlorine, potash, and oxide of iron are the most frequent. Its usual yellow or red colour is owing to the presence of some of the lower oxides of nitrogen. If pure, it leaves no fixed residue when evaporated on a slip of glass, and gives no precipitate when, after dilution with three or four times its bulk of water, it is tested for sulphuric acid with baric nitrate ( $Ba_2NO_3$ ), and for chlorine with argentic nitrate. By distilling it a second time, it may readily be obtained of specific gravity 1.42, and free from all impurities except the lower

\* Possibly a nitric chloro-dioxide is formed first, thus;  $2AgNO_3 + 2Cl_2 = 2AgCl + 2NO_2Cl + O_2$ , and then this nitric chloro-dioxide decomposes a second atom of argentic nitrate;  $AgNO_3 + NO_2Cl = AgCl + N_2O_5$ .



oxides of nitrogen. If chlorine be present, argentic nitrate may be added so long as the silver salt occasions a precipitate, or a silver coin may be dissolved in the acid; after which the rectification may be proceeded with. The lower oxides of nitrogen may be removed by diluting the acid with water till of a sp. gr. not exceeding 1.42, and then distilling with 2 or 3 per cent. of potassic dichromate.

**Nitrates.**—Nitric acid is monobasic; that is to say, each atom of nitron ( $\text{NO}_3$ ) requires one atom of a monad metal like potassium to neutralize it; the salts which it forms are termed *nitrates*. Their general formula is  $\text{M}'\text{NO}_3$ . These salts may be procured without difficulty by dissolving either the metal itself, or its oxide, or its carbonate, in nitric acid more or less diluted. Many of the nitrates, including those of potassium, sodium, ammonium, barium, lead, and silver, are anhydrous. Others combine with 6 atoms of water of crystallization; among these are the salts of magnesium, zinc, nickel, cobalt, iron, and copper; whilst in others the proportion of the water is different, calcic nitrate retaining  $4\text{H}_2\text{O}$ , and strontic nitrate  $5\text{H}_2\text{O}$ . If crystallized at a high temperature, cupric nitrate retains only  $3\text{H}_2\text{O}$ , and strontic nitrate may be obtained in the anhydrous form. No acid nitrates are known to exist, but several subnitrates or basic nitrates may be procured; that is to say, salts may be formed which contain more than one equivalent of basyl for each equivalent of acid radicle: such, for instance, as the hydrated basic nitrate of copper ( $\text{Cu}_2\text{NO}_3, 3\text{CuH}_2\text{O}_2$ ).

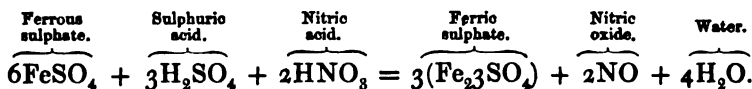
The following table gives the composition of some of the nitrates:

Potassic nitrate	...	...	...	...	$\text{KNO}_3$
Sodic nitrate	...	...	...	...	$\text{NaNO}_3$
Ammonic nitrate	...	...	...	...	$\text{H}_4\text{NNO}_3$
Baric nitrate	...	...	...	...	$\text{Ba}_2\text{NO}_3$
Strontic nitrate	...	...	...	...	$\text{Sr}_2\text{NO}_3, 5\text{H}_2\text{O}$
Calcic nitrate	...	...	...	...	$\text{Ca}_2\text{NO}_3, 4\text{H}_2\text{O}$
Magnesian nitrate	...	...	...	...	$\text{Mg}_2\text{NO}_3, 6\text{H}_2\text{O}$
Zincic nitrate	...	...	...	...	$\text{Zn}_2\text{NO}_3, 6\text{H}_2\text{O}$
Ferrous nitrate	...	...	...	...	$\text{Fe}_2\text{NO}_3, 6\text{H}_2\text{O}$
Cupric nitrate	...	...	...	...	$\text{Cu}_2\text{NO}_3, 6\text{H}_2\text{O}$
Plumbic nitrate	...	...	...	...	$\text{Pb}_2\text{NO}_3$
Argentific nitrate	...	...	...	...	$\text{AgNO}_3$
Mercurous nitrate	...	...	...	...	$\text{HgNO}_3, \text{H}_2\text{O}$
Hydrated plumbic subnitrate	...	...	...	...	$\text{Pb}_2\text{NO}_3, \text{PbH}_2\text{O}_2$
Hydrated cupric subnitrate	...	...	...	...	$\text{Cu}_2\text{NO}_3, 3\text{CuH}_2\text{O}_2$
Hydrated mercurous subnitrate	...	...	...	...	$3\text{HgNO}_3, \text{HgHO}$

Most of the nitrates fuse readily when heated: at an elevated temperature they are all decomposed. At first, from the nitrates of the alkali-metals, oxygen nearly pure escapes, and a nitrite is formed: afterwards the nitrite undergoes decomposition, a mixture

of oxygen and nitrogen passing off, and in most cases the pure oxide of the metal is left. When thrown on glowing coals, the nitrates are decomposed with scintillation: if paper be moistened with the solution of any nitrate, allowed to dry, and then burned, the smouldering combustion characteristic of touch-paper will be produced. This property is, however, also exhibited by the salts of some other acids, of which the chloric is the most important.

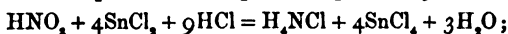
All the nitrates, when heated with sulphuric acid, evolve nitric acid; but there is no ready method of precipitating nitric acid from its solutions, since all its compounds are dissolved by water more or less freely. Various indirect methods have been proposed for ascertaining its presence. One of the best of these consists in neutralizing the solution, if acid, with potash, and evaporating nearly to dryness: then adding a few copper clippings, and heating the mixture with a little oil of vitriol: the copper decomposes the nitric acid if present, and characteristic red fumes of peroxide of nitrogen show themselves. A quantity of these fumes, too small to be visible, may be rendered evident by suspending in the vessel a piece of paper moistened with a mixture of starch and solution of potassic iodide, which will become blue from liberated iodine. A still smaller quantity of a nitrate may be detected by mixing a small quantity of a concentrated solution of ferrous sulphate with the liquor to be tested, and allowing the oil of vitriol to flow gradually into the solution so as to form a distinct stratum below it. In this case the characteristic action consists in the formation, at the line of contact between the two liquids, of a brownish-red solution, the colour of which disappears on boiling; the coloration depends upon the circumstance that the nitric oxide which is formed by the deoxidizing action of one portion of the iron salt, becomes dissolved with the distinctive brown colour, in the solution of the unoxidized part of the ferrous salt; the deoxidation of the nitric acid which occurs may be represented in the following equation:—



If a few drops of hydrochloric acid be added to a solution which contains free nitric acid, or a nitrate in solution, the liquid acquires the power of dissolving gold leaf. This effect, however, is produced by hydrochloric acid in solutions of the chlorates, bromates, and iodates; but the presence of these salts may be detected by other characters (382, 392, 397).

The accurate quantitative determination of nitric acid when mixed with other

acids is a matter of considerable difficulty. One method consists in the conversion of the acid into ammonia, and the subsequent determination of the amount of ammonia found (369). Another, which, when the quantity of nitric acid is very small, furnishes excellent results, is that proposed by Pugh (*Q. J. Chem. Soc.* xii. 35). It is based upon the determination of the amount of stannous chloride which is converted into stannic chloride when the solution is heated with nitric acid in presence of an excess of hydrochloric acid. A certain quantity of the concentrated solution containing the nitric acid to be determined is introduced into a strong tube, and a known volume of a solution of stannous chloride in a large excess of hydrochloric acid is added, the strength of the tin solution having been ascertained by the use of a standard solution of potassic dichromate. Care is taken to employ an excess of the tin solution. A fragment of marble is dropped into the tube so as to produce a quantity of carbonic anhydride sufficient to displace the atmospheric air. The tube is then carefully sealed and exposed for about a quarter of an hour to a temperature of  $338^{\circ}$  ( $170^{\circ}$  C.) It is allowed to cool, and the contents of the tube are next transferred to a glass and diluted with 90 or 100 cub. centim. of water; a few drops of a weak solution of potassic iodide and starch are then added, and the amount of tin still remaining in the form of stannous salt is determined by the addition of a graduated solution of the dichromate, until the liquid becomes blue from the liberation of iodine. The reaction upon which this process depends may be thus expressed:—



the nitrogen of the nitric acid being wholly converted into ammonia during the operation: the difference between the amount of the dichromate originally required to peroxidize the quantity of tin solution employed, and that actually consumed after the experiment is over, yielding the data for fixing the quantity of nitric acid: 393.3 mgrms. of the dichromate represent 63 of nitric acid ( $\text{HNO}_3$ ), or 54 of the anhydride,  $\text{N}_2\text{O}_5$ .

(364) **NITROUS OXIDE, or Protoxide of Nitrogen**;  $\text{N}_2\text{O} = 44$ . *Mol. Vol.*   ; *Rel. wt.* 22; *Theoretic Sp. Gr.* 1.5238; *Observed Sp. Gr.* 1.527.—*Preparation.*—1. If a mixture of equal parts of nitric and sulphuric acid, diluted with 8 or 10 parts of water, be digested on metallic zinc, the metal displaces hydrogen, which at the moment of its liberation deoxidizes the nitric acid, and a colourless gas is slowly given off, composed of 2 atoms of nitrogen united with 1 atom of oxygen.

2.—But to obtain the gas in a pure state it is far better to heat ammonic nitrate ( $\text{H}_4\text{NNO}_3$ , the salt furnished by neutralizing pure nitric acid with ammonic carbonate) in a glass retort; the salt quickly melts, and at a temperature of between  $392^{\circ}$  and  $500^{\circ}$  ( $200^{\circ}$  and  $260^{\circ}$  C.) apparently begins to boil, but in reality it is undergoing decomposition, by which it is entirely resolved into the gaseous nitrous oxide and steam. The temperature must be carefully watched, and not be allowed to rise so high as to occasion the production of white vapours in the retort, because the decomposition is then apt to occur with explosive violence. The reaction may be explained as follows:—Ammonium is a compound of nitrogen with hydrogen; when the ammonic nitrate is heated, the hydrogen of the ammonium combines with part of

the oxygen of the nitron, forming water, whilst the nitrogen of the ammonium at the same time becomes oxidized at the expense of another part of the oxygen of the nitron. The result is that the whole of the nitrogen, both of the nitron and of the ammonium, is liberated in the form of nitrous oxide:  $\text{H}_4\text{NNO}_3$  becoming  $2\text{H}_2\text{O} + \text{N}_2\text{O}$ ; 1 ounce or 30 grms. of the salt furnishes about 500 cubic inches, or rather more than 8 litres of the gas.

3.—L. Smith adopts a modification of the foregoing process for preparing the gas: he decomposes sal ammoniac ( $\text{H}_4\text{NCl}$ ) by means of nitric acid (of sp. gr. 1.20) at a gentle heat. The gas which is obtained in this manner is not pure, but is contaminated with small quantities of chlorine and of nitrogen; the chlorine may be removed by allowing the gas to bubble up through a solution of potash. Advantage may sometimes be taken of this action of nitric acid on sal ammoniac to destroy an excess of ammoniac chloride in solution in the course of an analysis.

*Properties.*—Nitrous oxide is a transparent, colourless gas, with a faint sweetish smell and taste: 100 volumes of water at  $32^\circ$  ( $0^\circ \text{C.}$ ) dissolve 130 of the gas; at  $59^\circ$  ( $15^\circ \text{C.}$ ), 77 vols.; and at  $75^\circ$  ( $24^\circ \text{C.}$ ) only 60 vols. (Bunsen). Owing to this considerable diminution in solubility with the rise of temperature, it should be collected over warm water. Under a pressure of 50 atmospheres at  $45^\circ$  ( $7^\circ \text{C.}$ ), it is reducible to a colourless liquid, of sp. gr. at  $45^\circ$ , of 0.908. It boils at about  $-126^\circ$  ( $-88^\circ \text{C.}$ ) (Regnault), and may be frozen into a transparent solid at about  $-150^\circ$  ( $-101^\circ \text{C.}$ ). When the liquid nitrous oxide was mixed with carbonic disulphide, and exposed to evaporation *in vacuo*, Natterer obtained a reduction of temperature which he estimated at  $-220^\circ$  ( $-140^\circ \text{C.}$ ); this is a lower point than has hitherto been attained by any other means. The gaseous nitrous oxide has a specific gravity of 1.527, which coincides with that of carbonic anhydride. This gas possesses the qualities neither of an acid nor of an alkali. It supports the combustion of many bodies with a brilliancy resembling that which they exhibit when burned in oxygen. It is, however, at once distinguished from oxygen by its considerable solubility in water. A glowing match bursts into flame when plunged into nitrous oxide: sulphur when kindled burns in it with a pale rose-coloured flame. A little nitric oxide is commonly formed during such combustions, and is manifested by the occurrence of ruddy fumes, due to admixture of this gas with the oxygen of the air as it enters the bottle.

Soon after the discovery of nitrous oxide, Davy ascertained that it may be respired for a few minutes: it then produces a

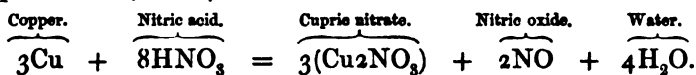
singular species of transient intoxication, attended in many instances with an irresistible propensity to muscular exertion, and often to uncontrollable laughter; hence the gas has acquired the popular name of *laughing-gas*.

*Composition.*—If nitrous oxide be passed repeatedly through a porcelain tube heated to bright redness, the gas is decomposed into a mixture of oxygen and nitrogen, 2 volumes becoming expanded permanently into the space of 3 volumes. An easy method of analysing nitrous oxide consists in mixing it with hydrogen, and passing an electric spark through the mixture. If 4 measures of nitrous oxide be mixed with an excess of hydrogen gas, say with 6 measures of hydrogen, in the bent eudiometer (fig. 290), 10 measures of mixed gas will be produced; and on transmitting the electric spark, inflammation will occur; steam will be formed by the oxidation of the hydrogen, and will be immediately condensed; the 10 measures will thus be reduced to 6: but the quantity of oxygen contained in the nitrous oxide cannot be at once inferred from this change of bulk: before this can be done, it is needful to ascertain how much hydrogen is left in the mixture. This may be effected by mixing the 6 remaining measures with 2 measures of oxygen, thus making 8 measures, and again transmitting the electric spark. Steam will again be formed, and immediately condensed: the 8 measures of the mixture will now be reduced to 5; 3 measures of the gas will therefore have disappeared, two-thirds of which, or 2 measures, are hydrogen: 1 measure of the gas now left must consequently be oxygen which was added in excess, and the remaining 4 measures are nitrogen. Of the 6 measures of hydrogen originally added, 4 have therefore combined with oxygen derived from the nitrous oxide; and since 4 measures of hydrogen require 2 measures of oxygen for conversion into water, the 4 measures of nitrous oxide must have contained 2 measures of oxygen. It appears, also, that nitrous oxide contains its own bulk of nitrogen, since the 4 measures of the gas originally employed furnish 4 measures of nitrogen; this nitrogen is moreover so combined with 2 measures of oxygen, that the 6 measures of the two gases when united are condensed into the space of 4 measures, or into two-thirds of the bulk which they occupied when separate. The specific gravity of the gas (1.527), found by experiment, shows that this conclusion is correct, and by calculation we find that such should be the case, for—

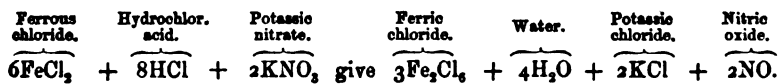
		By weight.	By vol.	Sp. gr.
Nitrogen	N <sub>2</sub> = 28	or 63.64	1.0 = 0.971	
Oxygen	O = 16	36.36	0.5 = 0.5528	
<hr/> Nitrous oxide	<hr/> N <sub>2</sub> O = 44	<hr/> 100.00	<hr/> 1.0 = 1.5238	

The proportion of nitrogen contained in the gas may also be ascertained by means of potassium; for if potassium be heated in nitrous oxide, it burns vividly, and is converted into potash, leaving a volume of nitrogen equal to that of the gas employed.

(365) **NITRIC OXIDE**; *Nitrosyl*; formerly *Deutoxide*, or *Bin-oxide*, of Nitrogen, ( $\text{NO}=\text{30}$ )\*; *Sp. Gr.* 1.039; *Atomic Vol.*  ; *Rel. wt.* 15.—*Preparation*.—1. If nitric acid be diluted with twice its bulk of water, so as to reduce it to a specific gravity of about 1.2, and be poured upon copper clippings or metallic mercury placed in a retort, brisk action speedily occurs; a gentle heat, if necessary, may be applied until it commences; the retort becomes filled with red fumes, and a gas is disengaged, which if collected over water will be found to be colourless; 1 ounce, or 30 grms., of copper by solution in about 120 c. c. of the diluted acid would yield nearly 420 cubic inches, or about 7 litres of nitric oxide. If the heat be too high the gas is apt to be contaminated with nitrogen. During this decomposition the metal may be supposed to displace hydrogen from one portion of the acid and form a nitrate, which is dissolved, whilst the hydrogen, in the moment of its liberation, decomposes another portion of the acid, forming water and setting nitric oxide at liberty. The following equation shows the reaction which occurs between 3 atoms of copper and 8 of nitric acid, resulting in the formation of 2 atoms of nitric oxide, 3 of cupric nitrate, and 4 of water:—



2.—Nitric oxide gas may also be obtained perfectly pure by digesting hydrochloric acid with iron filings till it will dissolve no more, decanting the clear liquid, and adding to it its own bulk of hydrochloric acid: on placing the solution in a retort, and adding potassic nitrate, the nitric oxide is immediately evolved in large quantity (Pelouze). The reaction is not so simple as in the preceding case; it may be represented as follows:—



A simple modification of this method consists in placing in a retort 30 grms. of commercial nitre, 240 grms. of ferrous sulphate, and pouring upon them 250 cubic centim. of diluted sulphuric acid

\* The vapour density of this compound is anomalous, NO yielding 2 volumes ( $\text{H} = 1$  vol.) instead of  $\text{N}_2\text{O}_2$ , as would be requisite if the compound followed the usual law.

(1 measure of acid to 3 measures of water). Such a mixture will give about 7 litres of pure nitric oxide.

*Composition.*—The composition of nitric oxide cannot be ascertained by detonation with hydrogen; for equal volumes of hydrogen and nitric oxide burn quietly with a green flame on the approach of a burning body. Davy analysed nitric oxide by heating charcoal strongly in it; 2 volumes of the gas by this treatment furnish 1 volume of nitrogen, and 1 volume of carbonic anhydride: but carbonic anhydride contains its own volume of oxygen; nitric oxide must therefore have consisted of 1 volume of nitrogen united without condensation with 1 volume of oxygen. The density of the gas (1.039) found by experiment confirms the correctness of this result, for by calculation,

			By weight.		By vol.	Sp. gr.
Nitrogen	N =	14	or 46.67	1 vol.	or 0.5 =	0.486
Oxygen	O =	16	53.33	1 vol.	0.5 =	0.552
Nitric oxide	NO =	30	100.00	2 vols.	1.0 =	1.038

Potassium burns when heated in the gas, potash being produced. If the experiment be conducted in such a manner as to allow the residual gas to be measured after the combustion is over, 2 volumes of nitric oxide will be found to leave 1 volume of nitrogen. A similar result is obtained when tin is heated in the gas.

*Properties.*—Nitric oxide has a strong disagreeable odour, and cannot be respired. It has hitherto resisted all attempts to liquefy it. Water does not dissolve more than one-twentieth of its bulk of this gas. Nitric oxide is the most stable of the oxides of nitrogen; it may even be exposed to a red heat without undergoing decomposition, but a succession of electric sparks converts it, if it be moist, into a mixture of nitrogen and nitric acid: and if digested upon moistened iron filings, or a moist sulphide of one of the alkali-metals, it is slowly converted into nitrous oxide. Many burning bodies, such, for instance, as a lighted taper, or phosphorus just kindled, are extinguished when plunged into the gas; but a decomposition of the gas will be effected if the phosphorus be burning vigorously, and it will deflagrate with a brilliancy equal to that produced by its combustion in oxygen. If a thin bulb containing a few drops of carbonic disulphide be placed in a jar of nitric oxide, closed by a glass plate, and agitated briskly, so as to break the bulb and diffuse the vapour through the gas, a mixture will be obtained which on the approach of a flame deflagrates with an intense white light.

Nitric oxide is completely absorbed by a solution of ferrous sulphate, with which it forms a deep reddish-brown liquid. All

the ferrous salts exert a similar action, and, according to Pélégot, 2 atoms of the salt of iron absorb 1 atom of nitric oxide, the solution in the case of the sulphate containing ( $2\text{FeSO}_4, \text{NO}$ ). The deep colour of the liquid thus formed is employed, as has already been mentioned (363), for the purpose of ascertaining the presence of nitric acid in solution. This liquid absorbs oxygen rapidly from the air or from gaseous mixtures; when heated, most of the nitric oxide is expelled from it unchanged. Solutions of stannous and mercurous salts also absorb nitric oxide, but they undergo change, and the gas cannot again be expelled from them by heat. Nitric acid likewise absorbs the gas rapidly: if the acid be concentrated, the solution becomes reddish brown; if more diluted, it is green; if still weaker, the solution is blue, but it diluted below a specific gravity of 1.15, little of the gas is absorbed, and the acid remains colourless.

Nitric oxide is neither acid nor alkaline in its characters. It has, however, a very powerful attraction for oxygen, and to this circumstance is owing one of the most characteristic properties of the gas:—when mixed with oxygen, or with any gas containing uncombined oxygen, dense red fumes are produced. These red fumes are freely soluble in water, and furnish an acid liquid. Formerly this circumstance was employed to determine the quantity of oxygen in mixture with other gases; but the method is now abandoned, as the absorption is not uniform, owing to the formation in uncertain quantity of a mixture of the soluble oxides of nitrogen. It may, however, be used with advantage as a qualitative test to demonstrate the existence of uncombined oxygen in a gaseous mixture. Nitric oxide also unites with half its volume of chlorine when the two gases are mixed, and nitrous oxychloride  $\text{NOCl}$  is formed (377).

(366) NITROUS ANHYDRIDE ( $\text{N}_2\text{O}_3=76$ ).—*Preparation.*—1. By mixing in an exhausted flask 4 volumes of nitric oxide with 1 volume of oxygen, both in a perfectly dry state, brownish-red fumes of nitrous anhydride are formed, which at a temperature of  $0^\circ$  ( $-18^\circ \text{C.}$ ) become condensed into a blue very volatile liquid, which emits a red vapour.

2.—Nitrous anhydride may also be obtained nearly in a state of purity, by heating in a capacious retort 1 part of starch with 8 parts of nitric acid of sp. gr. 1.25: it may be dried by passing it over calcic chloride, and may then be liquefied by transmission through a U-shaped tube surrounded by a mixture of ice and salt.

*Properties.*—A small quantity of water converts the anhydride into nitrous acid, but a larger quantity quickly decomposes it



into nitric acid and nitric oxide : hence the presence of a small quantity of water converts the blue into a dark green liquid, but a larger quantity decomposes it with effervescence : nitric acid is formed, and nitric oxide escapes. This last reaction may be thus represented :  $\text{H}_2\text{O} + 3\text{N}_2\text{O}_5$  give  $2\text{HNO}_3 + 4\text{NO}$ .

*Nitrites.*—Though in its uncombined form nitrous anhydride is decomposed by water with facility, yet nitrosion ( $\text{NO}_2$ ) forms permanent compounds with the metals of the alkalies : these salts are called *nitrites*. Their general formula is  $\text{M}'\text{NO}_2$ . If nitric oxide be placed over a solution of caustic potash, and small quantities of oxygen be added, potassic nitrite is produced in the liquid ; and if nitre, or sodic nitrate, be heated to redness until the gas which is evolved begins to contain nitrogen, the residue will be found to be composed chiefly of potassic or sodic nitrite. These nitrites are soluble in alcohol, and may thus be separated from the corresponding nitrates, which are insoluble. The normal nitrites of sodium, silver, and lead, are anhydrous. A considerable number of double nitrites of potassium may be formed. Lang has, for instance, among others, described the following :—

Nitrite of potassium	...	...	$2\text{KNO}_2, \text{H}_2\text{O}$
"	"	and barium	$2\text{KNO}_2, \text{Ba}_2\text{NO}_2, \text{H}_2\text{O}$
"	"	and zinc	$2\text{KNO}_2, \text{Zn}_2\text{NO}_2, \text{H}_2\text{O}$
"	"	barium and } nickel ... }	$2\text{KNO}_2, \text{Ba}_2\text{NO}_2, \text{Ni}_2\text{NO}_2$ .

If the nitrite either of potassium or of sodium be dissolved in water, and argentic nitrate be added, a sparingly soluble argentic nitrite is precipitated : by dissolving this precipitate in hot water, it is obtained pure in crystals as the liquid cools. The addition of cold diluted sulphuric acid to a solution of a nitrite decomposes the salt, and the liquid then becomes of a brownish-red colour on adding a solution of ferrous sulphate. The nitrites may thus be distinguished from the nitrates, since the latter do not change colour when similarly treated, unless heat be applied. A very minute trace of any nitrite may be detected by mixing a dilute solution of potassic iodide, free from iodate, with starch and a little diluted hydrochloric acid (sp. gr. 1.006) ; the liquid to be tested, after being acidulated with hydrochloric acid, is then to be added to the test mixture, when the blue colour of iodide of starch will appear, even when only traces of a nitrite are present. Acid solutions of the nitrites destroy the blue colour of indigo at ordinary temperatures, acting in this as in the preceding cases by its oxidizing powers ; but in other instances it shows reducing powers equally marked. Acidulated solutions of the nitrites, for

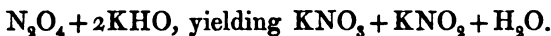
example, bleach potassic permanganate, and slowly reduce potassic chromate to a green salt of chromium. The auric chloride is reducible to metallic gold by these salts, and mercurous salts give with a nitrite a grey precipitate of reduced mercury.

The presence of nitrites in the well waters of towns is of common occurrence, probably owing to the oxidation of ammonia. Nitrous acid is formed from ammonia, when the latter is in contact with atmospheric air in the presence of platinum black, or of a coil of heated platinum wire; if a coil of red-hot platinum wire be held in a jar of air moistened with a few drops of a strong solution of ammonia, white fumes of ammoniac nitrite will be formed. The contact of metallic copper is still more effectual in promoting the formation of nitrous acid from ammonia, when free oxygen is present; if a small quantity of pulverulent copper be shaken up in a bottle of air, with a few drops of a solution of ammonia, the oxygen will be absorbed in a few minutes, and nitrous acid will be found in the liquid. Even bright slips of copper effect a similar oxidation of the ammonia, whilst oxide of copper is formed simultaneously. The cause of these phenomena is obscure; they belong to the class of actions commonly known as catalytic. According to Schönbein, the white fumes produced during the spontaneous oxidation of phosphorus in air consist, not of phosphorous anhydride, but of ammoniac nitrite formed by the action of the ozone upon moist air.

Schönbein has shown that the solutions of the nitrates of the alkali-metals, as well as some other nitrates, may be reduced slowly to nitrites by stirring or agitation with a rod of zinc or of cadmium, the reduction being accelerated by heat.

(367) PEROXIDE OF NITROGEN; *Nitric peroxide* or *Hyponitric acid*,  $N_2O_4=92$ , or  $NO_2=46$ ; *Melting-pt.*  $18^\circ$  ( $-9^\circ$  C.), Pélilot; *Boiling-pt.*  $71^\circ$  ( $22^\circ$  C.).—*Preparation.*—1. The red fumes which appear on mixing nitric oxide with atmospheric air consist mainly of peroxide of nitrogen. The peroxide may be procured in prismatic crystals by passing two volumes of nitric oxide and 1 of oxygen, both perfectly dry, into tubes previously dried with scrupulous care, and cooled down by a mixture of ice and salt. (Pélilot, *Ann. de Chimie*, III. ii. 61.) These crystals melt at  $18^\circ$  F.; at the ordinary temperature of the air they form an orange-coloured liquid, which boils at  $71^\circ$ , and produces a deep brownish-red vapour. It is remarkable that after this compound has once been melted it does not freeze even at  $0^\circ$  ( $-18^\circ$  C.). This substance is decomposed by water with singular facility; a minute trace of water is sufficient to prevent the formation of the

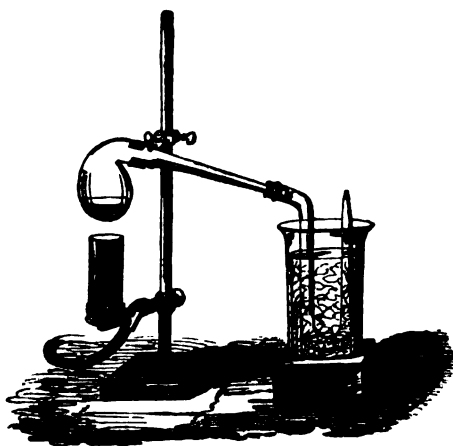
crystalline compound, occasioning in its stead the production of a green liquid (probably  $N_2O_3, N_2O_5, H_2O$ ), similar to that obtained by the distillation of plumbic nitrate. The peroxide of nitrogen was long considered to possess acid properties, and hence was termed hyponitric acid. It, however, does not form specific salts, but is immediately decomposed by bases into a nitrate and nitrite:—



But when the liquid peroxide is digested on a metal, such as potassium, lead, or mercury, nitrate of the metal is formed, and nitric oxide is expelled; with potassium for instance,  $K + N_2O_4 = KNO_3 + NO$ . No nitrite is formed under these circumstances.

2.—If plumbic nitrate ( $Pb_2NO_3$ ) be dried, and heated strongly in a small glass retort, it is decomposed; deep red fumes, consisting of a mixture of peroxide of nitrogen and free oxygen are produced, and plumbic oxide is left:  $2(Pb_2NO_3) = 2PbO + 2N_2O_4 + O_2$ . If the red vapour be made to pass through a bent tube

FIG. 301.



surrounded by ice and salt, as shown in fig. 301, the peroxide is condensed to a liquid which is green, owing to the presence of a little moisture. Towards the latter part of the distillation the anhydrous peroxide comes over, and if the receiver be changed, it may be obtained in crystals. The melted peroxide is nearly colourless at  $0^\circ$  ( $-18^\circ C.$ ): it becomes yellow at  $14^\circ$  ( $-10^\circ C.$ ), and at or-

ordinary temperatures is red. It has a specific gravity of 1.451, boils at  $82^\circ$  ( $28^\circ C.$ ; Müller), and freezes at  $-40^\circ$ . It emits a dense brownish-red vapour, which becomes deeper in tint as the temperature rises, till at  $100^\circ$  ( $38^\circ C.$ ) it is almost opaque.

Playfair and Wanklyn have shown it to be probable that at low temperatures the compound has the formula  $N_2O_4$ , but that as the temperature rises it assumes the constitution  $NO_2$ . Müller (*Lieb. Ann.* cxxii. 15) finds the sp. gr. of the vapour, at  $82^\circ$  ( $28^\circ C.$ ) to be 2.70;  $N_2O_4 = \square$  theoretically would give 3.18; whilst at  $170^\circ$  ( $77^\circ C.$ ) the sp. gravity of the vapour is only 1.84; and Mit-

schcrlich, at some temperature not stated, but probably higher, found it as low as 1.71; the calculated density for the formula  $\text{NO}_3 = \square$  is 1.591.

This will be seen by the following table:—

	By weight.		By volume.		
Nitrogen	N = 14	or 30.44	1	or 0.5	= 0.486
Oxygen	O <sub>2</sub> = 32	69.56	2	1.0	= 1.105
<hr/>					
Peroxide of nitrogen } $\text{NO}_3 = \square$	46	100.00	2	1.0	1.591
					<hr/>
					$\text{N}_2\text{O}_4$ 2    1.0    3.183

This vapour has a peculiar, suffocating odour. It supports the combustion of a taper, and of many burning bodies; potassium takes fire in it spontaneously. If water be added gradually to the liquid peroxide, it passes through various tints, becoming successively orange, yellow, green, blue, and finally colourless, an effervescence being occasioned during the whole time from the escape of nitric oxide; finally, nitric acid in abundance is formed in the liquid;  $\text{H}_2\text{O} + 3\text{NO}_3 = \text{NO} + 2\text{HNO}_3$ . The nitric oxide, on mixing with the oxygen of the air, reproduces the peroxide of nitrogen as usual. The different tints assumed by the liquid during dilution appear to be owing to the solution of the nitric oxide in varying proportion in the nitric acid produced by the decomposition. Peroxide of nitrogen combines directly with hydrochloric acid, and forms several chlorinated compounds (377). It also is absorbed by concentrated sulphuric acid, and forms a crystalline compound with it ( $2\text{H}_2\text{SO}_4, \text{N}_2\text{O}_4, \text{SO}_3$ ; 412 note).

Peroxide of nitrogen may be distinguished from nitrous acid by its power of imparting to a neutral solution of potassic sulphocyanide a red tint closely resembling that produced in the same reagent by ferric salts; in a few minutes, however, the decomposition proceeds further, and the liquid becomes colourless.

(368) The important influence of proportion upon the products of chemical combination is exhibited in a striking light by these compounds of nitrogen with oxygen. The same elements, according to the quantities in which they are united, may, as in nitric acid, produce one of the most corrosive compounds in the range of chemistry; or may give rise, as in the case of the nitrous oxide, to a stimulating and intoxicating gas, which may be breathed with impunity; while the intermediate combinations exhibit properties entirely different from either. A broad distinction may also be easily traced between the results of mixture and those of true chemical union. The properties of the atmosphere are the results of simple admixture: the chemical qualities of oxygen appearing to be simply diluted by its apparently inert companion, nitrogen

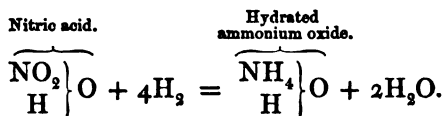
(just as the sweetness of sugar is reduced by the addition of water); whilst each one of the true combinations of nitrogen with oxygen exhibits characters distinct from those of either of its components.

### § II.—COMPOUNDS OF NITROGEN WITH HYDROGEN.

AMMONIA, *Volatile Alkali, or Spirit of Hartshorn* ( $\text{H}_3\text{N}=17$ ).  
*Melting-pt.*  $-103^\circ$  ( $-75^\circ \text{C.}$ ); *Boiling-pt.*  $-37^\circ$  ( $-38^\circ \text{C.}$ ); *Theoretic Sp. Gr.* 0.5896; *Observed Sp. Gr.* 0.59; *Atomic and Mol. Vol.*  $\square\square$ ; *Rel. wt.* 8.5.

(369) THIS important compound has received the name of ammonia, from the circumstance of its having been obtained from a salt first procured in Libya, near the temple of Jupiter Ammon, and hence termed sal ammoniac. Nitrogen and hydrogen do not combine directly with each other; nevertheless, their indirect combination is a circumstance of continual occurrence. The spontaneous decomposition of moist animal matters, which contain both hydrogen and nitrogen, and almost every process of oxidation in the presence of moisture, is attended with the formation of ammonia. The hydrogen, at the moment of its liberation from the water by deoxidation, appears to enter into combination with the nitrogen of the atmosphere, which, to a small extent, is held in solution, and thus ammonia is formed. If a current of nitric oxide be transmitted over a mixture of potassic hydrate and slaked lime, nitrates of potassium and calcium are formed, while ammonia is generated. Moistened iron filings, if exposed to the air, become rusty, and the oxidized compound retains a small quantity of ammonia.

The deoxidation of dilute nitric acid by the metals also frequently gives rise to the production of ammonia; two atoms of oxygen changing places with four of hydrogen:—



Tin, zinc, and iron exhibit this effect in a marked degree (p. 94). This reaction has been used as a means of estimating the quantity of nitric acid in solutions; for by dissolving zinc very slowly in diluted hydrochloric acid, and adding the nitric solution in small quantities at a time, the whole of the nitric acid is converted into ammonia. (Nesbit, *Q. J. Chem. Soc.* i. 281.) Harcourt has improved upon this method (*J. Chem. Soc.* 1862, xv. 381);

he distils the concentrated liquid with caustic potash and a mixture of granulated zinc and iron turnings, and receives the distillate containing the ammonia into a known weight of a standard solution of sulphuric acid.

When a mixture of 2 volumes of nitric oxide and 5 of hydrogen is transmitted over spongy platinum or platinized asbestos gently heated, water and ammonia are produced. Hadow has also observed the formation of ammonia when nitrous acid or peroxide of nitrogen is reduced by transmitting either of them through a solution of hydropotassic sulphide (KHS) or through one of ferrous acetate.

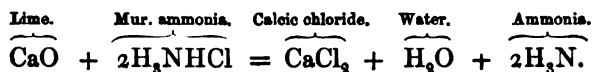
Ammonia exists in minute quantity in the atmosphere.

According to the elaborate researches of Ville, which appear to have been conducted with every precaution to ensure accuracy, one million kilogrammes of air contained on the average, in the year 1849, 2.47 grms. of ammonia, and in 1850, 21.1 grms. This amounts to about one volume of ammonia in twenty-eight million volumes of air, or 0.035 c. c. of the gas in 1 cubic metre of air. Other experimenters make the quantity considerably higher. The proportion of ammonia contained in rain water is liable to considerable variation: in 1,000,000 parts of rain water collected in Paris during the last five months of 1851, Barral found 3.49 parts; Boussingault, at Liebfraunberg, in 1852, found only 0.744 parts; and Lawes and Gilbert, at Rothamsted, in 1853 and 1854, found the average amount from March to August to be 1.142, from September to February 0.927 parts: the average of the last two determinations would give about 1 grain of ammonia in 14 gallons of rain water, or about 1 gramme of ammonia in a cubic metre of rain water. Boussingault has corroborated Barral's results by experiments upon the rain collected in Paris; indeed it is not surprising that in a populous city, crowded with animal life, and with the exuviae of animals, the proportion of ammonia in its atmosphere should be much higher than in the surrounding districts. It appears, also, that a larger quantity of ammonia is always contained in the water that is collected at the commencement of a shower than at the end of it, and more after a drought than after a period of rainy weather. In the water of dews and fogs, also, the amount of ammonia was found to be much higher than in rain water. The proportion of ammonia in water derived from the atmosphere is, in short, greater, the smaller the fall, a circumstance which is easily accounted for by the high solubility of the gas in water. The atmospheric supply of ammonia is intimately connected with the storing of nitrogen in plants.

Ammonia is also found in clayey and in peaty soils, both of which absorb it freely. When azotised matters are heated with the hydrated alkalis, they are decomposed, and the whole of the nitrogen, unless present in the form of a nitrate or a cyanide, is disengaged as ammonia; upon this fact is based the usual method of determining the amount of nitrogen in organic compounds. For the purposes of manufacture ammonia is, however, always procured by the distillation, in closed vessels, of organic matters containing nitrogen. During the distillation of bones, and of animal refuse generally, ammonia in considerable quantity is formed, and condensed along with the foetid products of the operation.

But the principal part of the ammonia used in the country is obtained from the refuse products of the distillation of coal for the manufacture of gas. Amongst these products are water, and a considerable quantity of carbonate and sulphide of ammonium; the ammoniacal salts become dissolved in the water, and constitute the ammoniacal liquor of the gas-works; this liquor is saturated subsequently with sulphuric or with hydrochloric acid, and thus ammonic sulphate or chloride (the sulphate or muriate of ammonia of commerce) is procured (617).

*Preparation.*—If equal weights of quick-lime and either the sulphate or muriate of ammonia be separately powdered and intimately mixed, the powder, on being transferred to a retort and gently heated, gives off abundance of pure ammonia, as a transparent, colourless gas, of the peculiar, pungent odour of smelling salts; 1 ounce of muriate of ammonia, if fully decomposed, would yield about 750 cubic in., or 30 grms. about  $12\frac{1}{2}$  litres of the gas. The lime combines with the acid and sets the ammonia at liberty, calcic chloride, and water being formed; the result when muriate of ammonia is used admitting of representation as follows:—



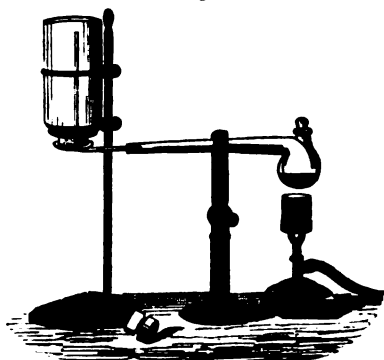
*Properties.*—Ammonia produces a flow of tears from the eyes; it has an acrid taste, and, when breathed in a concentrated form, is fatal to life, from its irritating effects on the lungs. In a more diluted form it is a highly valuable stimulant.

Ammonia does not support the flame of burning bodies, but is feebly combustible; a jet of the gas directed across the stream of hot air issuing from a lighted argand lamp, burns with a very pale green flame, and a jet of the gas may be kindled readily in an atmosphere of oxygen. If the gas be mingled with an equal bulk of oxygen, the mixture may be detonated by means of the electric spark; water, nitrogen, and traces of nitric acid are formed. If a mixture of ammonia and air or oxygen be passed over spongy platinum, water and nitric acid are amongst the products. If a stream of ozonized air be transmitted into a bottle containing a small quantity of a concentrated solution of ammonia, dense white fumes of ammonic nitrite are formed, owing to the partial oxidation of ammonia by the ozone.

Ammonia is extremely soluble in water, and must therefore be collected either over mercury, or by displacement, in the manner shown in fig. 302. The latter mode of collecting it may easily be effected, as the gas has little more than half the density

of atmospheric air, its sp. gr. being only 0.59. Ammonia has a powerfully alkaline reaction, and turns turmeric paper brown. When collected by displacement, the gas must be allowed to pass into the bottle until a piece of dry turmeric paper held to the mouth of the bottle is immediately turned brown; the tube is then withdrawn, and the stopper, slightly greased, is inserted.

FIG. 302.



Ammonia neutralizes the most powerful acids, and forms a very important class of salts. Any volatile or gaseous acid brought into an atmosphere containing ammonia, produces a white cloud, owing to the formation of a solid salt. This property is often employed to detect small quantities of ammonia: slaked lime or potassic hydrate is mixed with the solution suspected to contain ammonia, and the whole gently warmed in a tube; a rod moistened with hydrochloric acid diluted with half its bulk of water is then placed in the upper part of the tube or vessel, and if ammonia be present, white fumes appear, even when the quantity of ammonia is too small to be distinguished by the smell. When ammoniacal gas is required in a state free from moisture it must be transmitted over quick-lime, not over calcic chloride; for this salt, as well as many other saline compounds, absorbs ammonia and forms with it a definite compound (622).

Ammoniacal gas may be liquefied by exposure to a cold of  $-40^{\circ}$ , or still more readily by generating it under the pressure of its own atmosphere. The easiest method is the following:—

Argentic chloride in powder is exposed to a current of dry ammoniacal gas; the ammonia is rapidly absorbed, and the chloride increases in weight more than one-third. This substance is placed in one limb of a strong tube bent to an obtuse angle, and then hermetically sealed; on applying heat to the chloride, and cooling the other end of the tube with a freezing mixture, the ammonia is condensed as a colourless liquid, which boils at  $-38^{\circ}$  (Regnault), exerts a pressure of 6.9 atmospheres at  $60^{\circ}$  ( $15^{\circ}.5$  C.), and has a specific gravity of 0.731 (Faraday; or 0.614, Andreëff). By a cold of  $-103^{\circ}$  ( $-75^{\circ}$  C.), it is frozen to a white, translucent, crystalline solid, which is denser than the liquid. The argentic chloride re-absorbs the liquefied ammonia at ordinary temperatures, and slowly reproduces the original compound.

*Composition.*—The composition of ammonia may be ascertained as follows:—If the dry gas be subjected to a succession of electric sparks, by the aid of Ruhmkorff's coil, or if it be passed slowly through a porcelain tube containing iron or copper turn-



ings, heated to bright redness, the gas is decomposed; it becomes dilated to double its volume: 4 volumes of ammonia become 8; and the gas produced may be shown, by detonating a portion of it with oxygen, to consist of a mixture of 2 volumes of nitrogen with 6 of hydrogen. If, after adding 8 measures of this mixture in the bent eudiometer to 4 of oxygen, so as to make 12 measures in the whole, the electric spark be transmitted, 3 measures will be left, owing to the formation of steam and its subsequent condensation. Since in the formation of water 2 measures of hydrogen combine with 1 measure of oxygen, one-third of the volume of gas which has disappeared, or 3 measures, will be oxygen, and two-thirds, or 6 measures, will be hydrogen. On agitating the residual gas with a solution of potassic hydrate, no change of bulk will occur, consequently no carbonic anhydride can have been formed; but on the addition of pyrogallic acid (*note*, p. 65) to the gas whilst still in contact with the alkaline liquid, the excess of oxygen will be absorbed. This will amount to 1 measure, whilst 2 measures of nitrogen remain unacted upon; 2 measures of nitrogen must therefore have been present in the ammonia in combination with 6 of hydrogen which have become condensed as steam; consequently, since the ammonia doubles its volume when decomposed by heat, the 4 volumes of ammonia must have been formed by 6 volumes of hydrogen and 2 of nitrogen, condensed into half their bulk. The composition of ammonia may therefore be thus represented:—

		By weight.	By vol.	Sp. gr.
Hydrogen	$H_2$	= 3 or 17.65	3 or 1.5	= 0.1036
Nitrogen	N	= 14 82.35	1 0.5	= 0.4860
Ammonia	$H_2N$	17 100.00	2 1.0	0.5896

Other striking proofs of the composition of ammonia are afforded by the action of heat upon some of its salts. The decomposition of ammonic nitrate offers one of these: by the action of heat, as already explained (364), the ammonic nitrate ( $H_4NNO_3$ ) is decomposed into water and nitrous oxide,  $2H_2O + N_2O$ ; the 4 atoms of hydrogen in the ammonium combining with 2 of oxygen in the nitron, and leaving the nitrogen of the ammonia to combine with nitric oxide derived from the nitron. If a solution of ammonic nitrite be heated, the salt is decomposed, water and pure nitrogen are liberated: the result may be thus represented,  $H_4NNO_2 = 2H_2O + N_2$ : the hydrogen of the ammonium is in this case exactly sufficient to combine with the oxygen of the nitrosion ( $NO_2$ ), forming water: this is an

excellent mode of obtaining pure nitrogen. When nitrogen is to be procured in this way, the most convenient method consists in preparing potassic nitrite by saturating a solution of caustic potash of sp. gr. 1.38, with nitrous acid disengaged by acting upon starch with nitric acid of sp. gr. 1.25. This solution, if it be left slightly alkaline, may be preserved without alteration. When it is wanted for the preparation of nitrogen, the liquid is to be mixed with three times its bulk of a saturated solution of sal ammoniac, and gently heated in a small retort: nitrogen is evolved abundantly, and with great regularity (Corenwinder).

Nitrogen may also be prepared by heating muriate of ammonia in fine powder, intimately mixed with potassic dichromate, in which case the reaction may be thus represented;  $K_2Cr_2O_7 + 2H_4NCl = Cr_2O_3 + 4H_2O + 2KCl + N_2$ .

Chlorine also decomposes ammonia at ordinary temperatures, and liberates nitrogen gas. Under certain circumstances it produces the detonating compound known as chloride of nitrogen (386). Bromine and iodine likewise decompose ammonia, and form similar detonating compounds, without producing any liberation of nitrogen.

(370) *Solution of Ammonia*.—A solution of ammonia in water is a reagent continually required in the laboratory. When ammoniacal gas is passed into water it is rapidly absorbed, with considerable extrication of heat; at a temperature of 32°, Carius found that water takes up about 1050 times its volume of the gas; at 59°, 727 times its volume; and at 78° (26° C.) 586 times its volume: water saturated with ammonia at 60° (15°.5 C.) contains more than one-third of its weight of the gas, increasing in bulk nearly one-half, and becoming specifically lighter. The following table indicates the strength of solutions of pure ammonia of different specific gravities:—

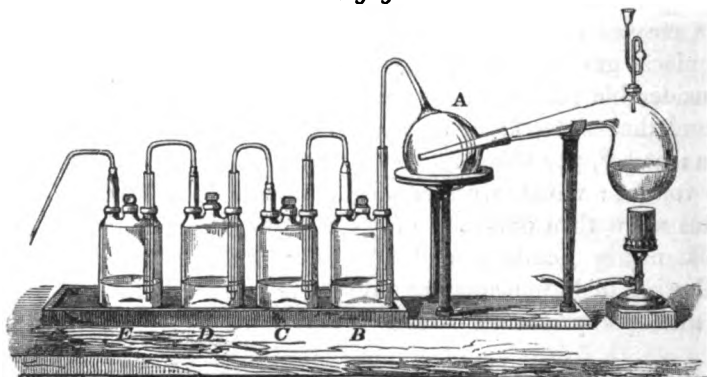
*Strength of Solutions of Ammonia at 57° (14° C.) (Carius.)*

Ammonia in 100 parts by weight.	Specific gravity.	Ammonia in 100 parts by weight.	Specific gravity.	Ammonia in 100 parts by weight.	Specific gravity.	Ammonia in 100 parts by weight.	Specific gravity.
36	0.8844	27	0.9052	18	0.9314	9	0.9631
35	0.8864	26	0.9078	17	0.9347	8	0.9670
34	0.8885	25	0.9106	16	0.9380	7	0.9709
33	0.8907	24	0.9133	15	0.9414	6	0.9749
32	0.8929	23	0.9162	14	0.9449	5	0.9790
31	0.8953	22	0.9191	13	0.9484	4	0.9831
30	0.8976	21	0.9221	12	0.9520	3	0.9873
29	0.9001	20	0.9251	11	0.9556	2	0.9915
28	0.9026	19	0.9283	10	0.9593	1	0.9959

Solution of ammonia is colourless and intensely alkaline ; it has an acrid, caustic taste, and blisters the skin if applied to it in a concentrated form ; it freezes at about  $-40^{\circ}$ , yielding a gelatinous mass, destitute of odour. Simple exposure of the solution at ordinary temperatures to the air is attended with an escape of the gas, which occasions the pungent smell of the liquid. By heat the ammonia is expelled rapidly, with the appearance of ebullition, thereby furnishing a ready extempore method of procuring the gas. By heating the liquid for some time, the whole of the ammonia may be driven off, so that nothing but water is left in the retort.

Solution of ammonia is prepared on the large scale by mixing together in a capacious retort equal weights of well-burned quicklime and sal ammoniac ; the lime is slaked and made into a paste with water before mixture. The retort is then connected with a series of bottles similar to those used for condensing nitric acid. If the operation be conducted on the small scale in the laboratory, the arrangement shown in fig. 303 may be adopted. The three-

FIG. 303.



necked bottles, B, C, D, E, are known by the name of Woulfe's bottles : in the globe, A, a small quantity of water is placed, to retain any solid particles which may be mechanically carried over by the gas ; in the first bottle, B (which may be kept cool by immersion in cold water), a quantity of water equal in weight to that of the sal ammoniac used is introduced, taking care that it shall not fill more than half the capacity of the bottle, whilst the second contains water to condense any gas that may escape through the first. Each bottle is provided with a safety tube open at both ends, so that if the gas were absorbed in B, for example, more rapidly than it was supplied, instead of the liquid

being driven back from the bottle, c, air would enter by the safety tube, and the equilibrium would be restored. The tube which delivers the gas passes down through the safety tube, and projects a little beyond its lower opening, so that the gas rises in bubbles through the liquid and collects in the bottle; an air-tight joint, which can be mounted and dismounted immediately, is thus obtained.

Solution of ammonia, if pure, should, when evaporated, leave no solid residue; the presence of carbonic acid may be detected by lime-water, which it renders milky; that of chlorine by acidulating slightly with pure nitric acid, and adding argentic nitrate, when it gives a white cloud; that of sulphuric acid by a white precipitate with baric nitrate after dilution and saturation with nitric acid; that of lime by a white precipitate on adding ammoniac oxalate; and that of copper or lead derived from the apparatus, by a black or brown precipitate or cloud with sulphuretted hydrogen. Lead in small quantity is a very frequent impurity in the commercial solution; it is usually derived from the action of the ammonia on the flint glass bottles in which it is often improperly kept.

Alcohol also dissolves ammonia in abundance.

The salts of ammonia will be described with those of the other alkalies, and the tests for ammonia will be given at the same time.

(371) AMIDOGEN? ( $H_2N=16$ ).—Ammonia is the only compound of hydrogen and nitrogen that has been obtained in the isolated form. When, however, potassium is heated gently in perfectly dry ammoniacal gas, the ammonia disappears, half its volume of hydrogen is liberated, and a fusible, olive-green compound is formed, consisting of  $KH_2N$ . The ammonia is decomposed by the potassium in the following manner:  $2H_3N + K_2$  becomes  $2KH_2N + H_2$ . The compound  $H_2N$  has received the name of *amidogen*, and is supposed by some chemists to be capable of existing in combination with several metals and with a variety of bodies derived from the organic kingdom, though late researches have rendered it more probable that all these bodies are to be regarded as substitution-products formed upon the type of ammonia. Compounds of this class have received the name of *amides*; they will be more conveniently examined hereafter.

AMMONIUM ( $H_4N=18$ ).—This compound, as is the case with amidogen, has not been obtained in a separate form. All the usual so-called salts of ammonia, however, appear to contain it. Ammonic nitrate, for example, when formed by the action of ammonia on nitric acid, is not accompanied by any separation

of the elements of water, which cannot be expelled by heat without the entire decomposition of the salt (364);  $\text{H}_3\text{N} + \text{HNO}_3$  becoming  $\text{H}_4\text{N}\cdot\text{NO}_3$ . Sal ammoniac is on this view regarded as ammoniac chloride  $\text{H}_4\text{N}\cdot\text{Cl}$ . The full discussion of the grounds upon which this theory rests will be best postponed till we enter upon a description of the salts of ammonia (610 *et seq.*)\*

## CHAPTER VI.

## THE HALOGENS.

(372) BEFORE proceeding to notice some other compounds of the four elements already described, it will be desirable to examine the other non-metallic simple substances. We pass on, therefore, to a group of four closely allied bodies, viz., chlorine, bromine, iodine, and fluorine, all of which are monads. These elements are characterized by the powerful activity of their chemical attraction for other substances at the ordinary temperature of the air; and consequently none of them are found in an uncombined state. They form with the metals compounds analogous to sea salt, and have hence been termed *halogens*, or salt-producers (from  $\alpha\lambda\gamma$ , sea salt).

§ I. CHLORINE:  $\text{Cl} = 35.5$ ; *Theoretic Sp. Gr.* 2.453; *Observed Sp. Gr.* 2.47; *Atomic Vol.*  $\square$ ;  $\dagger$  *Rel. wt.* 35.5; *Monad, as in HCl.*

(373) CHLORINE, the most important member of the group of halogens, was discovered by Scheele in 1774. It is abundantly met with in combination with sodium, with which it constitutes ordinary table salt. This necessary of life occurs plentifully in beds in various parts of the world, and is the most abundant of the saline bodies contained in the waters of the ocean. It contains 60.68 per cent. of chlorine.

*Properties.*—Chlorine is a transparent gas of a greenish-yellow colour (whence the name is derived, from  $\chi\lambda\omega\rho\delta\varsigma$ , green),

\* A base to which the name of *hydroxylamine* ( $\text{H}_2\text{ON}$ ) has been given, was discovered by Lossen, amongst the products of the decomposition of nitric ether. It furnishes crystallizable salts.

$\dagger$  Gaseous chlorine is now regarded as chloric chloride, and consequently its molecular volume is  $(\text{ClCl}) = 2$  vols. or  $\square\square$ , and its *molecular weight* = 71. The molecular volume of all the halogens in their free state will be 2, if that of chlorine be so regarded; the free substances being viewed respectively as fluoric fluoride, bromic bromide, and iodic iodide.

and of a powerful suffocating odour, producing, if breathed, even when largely diluted with air, distressing irritation of the air passages, attended with coughing. It is much heavier than air; a litre at  $0^{\circ}\text{C}$ . and  $760^{\text{mm}}$ . weighs  $3.208$  grms., or  $100$  cubic inches at  $60^{\circ}\text{F}$ . and  $30$  inches Bar. weigh between  $77$  and  $78$  grains. Under a pressure of  $4$  atmospheres at  $60^{\circ}$ , it is condensed to a yellow limpid liquid, of sp. gr. about  $1.33$ ; it does not conduct electricity, and remains unfrozen even at the cold of  $-220^{\circ}$  ( $-140^{\circ}\text{C}$ ). Chlorine is soluble in about half its bulk of cold water; this solution, which is readily formed by agitating the gas and water together, has the colour, odour, and astringent taste of the gas. According to Schönfeld, water at  $50^{\circ}$  ( $10^{\circ}\text{C}$ .) dissolves  $2.585$  times its bulk of the gas; at  $59^{\circ}$ ,  $2.368$ , and at  $104^{\circ}$  ( $40^{\circ}\text{C}$ .)  $1.365$  times its bulk. Chlorine, in consequence of this solubility, cannot be advantageously collected over cold water. Mercury is acted upon by the gas with great rapidity. It is necessary, therefore, either to use warm water in the pneumatic trough, or to receive the gas by the process of displacement in dry bottles. With water, chlorine forms a definite *hydrate* ( $\text{Cl}_2\cdot 5\text{H}_2\text{O}$ ), which crystallizes at  $32^{\circ}$  ( $0^{\circ}\text{C}$ .); this, if it be enclosed in hermetically sealed tubes, furnishes a ready method of obtaining liquefied chlorine, since it is easily decomposed by a gentle heat into water and free chlorine; the latter amounts to about one-fourth of the volume of the liquid.

Chlorine is not combustible, and it does not combine directly with oxygen. A taper burns in it with a reddish, smoky flame, the hydrogen of the combustible vapour of the wax combining with the chlorine, whilst part of the carbon, for which its chemical attraction is but small, is deposited. Many bodies, however, take fire spontaneously when introduced into chlorine; this is the case with phosphorus: many of the metals in a finely divided state do the same; among them are copper leaf, finely powdered antimony, and arsenicum. A great number of organic substances rich in hydrogen are decomposed by chlorine, sometimes with such rapidity as to inflame them; a bit of paper dipped into oil of turpentine and plunged into the gas bursts into flame, and deposits an abundance of a black carbonaceous compound.

The action of chlorine upon bodies containing hydrogen is often of a very peculiar kind. It combines with part of the hydrogen and withdraws it from the combination; each atom of hydrogen uniting with an atom of chlorine, and forming a powerful acid, the hydrochloric ( $\text{HCl}$ ); whilst at the same time for each atom of hydrogen so withdrawn from the original compound,

an atom of chlorine is substituted. It is in this way that chlorine exerts those bleaching powers which have rendered so essential a service to the calico-printer and the paper-maker. Most of the vegetable colouring matters contain hydrogen, and are decomposed by chlorine, whilst colourless, or nearly colourless, compounds containing chlorine are formed instead of the coloured compounds with hydrogen. If a solution of chlorine be mixed with some of the blue liquid formed by dissolving indigo in sulphuric acid, or with ordinary writing ink, or with tincture of litmus, the colour will in each case be immediately and almost completely discharged, and it cannot be subsequently restored.

Another property of chlorine of great value is its disinfecting power,—by which is meant its power of destroying noxious vapours and miasmata; with this view it is frequently employed for fumigating buildings after the occurrence of contagious diseases.

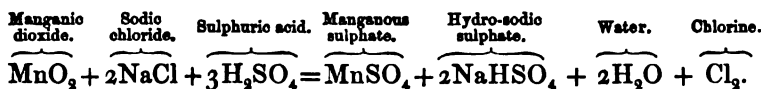
*Extraction.*—1. The preparation of gaseous chlorine is practised on an enormous scale in the manufacture of bleaching powder, or chloride of lime. It is generally prepared in capacious stills, sufficiently large to hold 200 gallons or about 900 litres of liquid; these are usually made of Yorkshire flags clamped together with ironwork, and the joints rendered tight by vulcanized caoutchouc. The lower part of these stills is enclosed in a case through which a current of steam is transmitted. Hydrochloric acid in solution, of specific gravity from 1·160 to 1·170 (which is obtained as a waste product in the manufacture of sodic carbonate from sea salt), is run through a curved funnel into the stills, previously charged with oxide of manganese in small lumps. The hydrogen of the acid is wholly converted into water by the oxygen of the oxide of manganese, one-half of the chlorine combining with the manganese whilst the other half escapes in the gaseous form; the reaction is illustrated by the following symbols:—



This process may also often be resorted to on the small scale in the laboratory with advantage. Three ounces or 100 grms. of powdered oxide of manganese with half a pint (350 cub. centim.) of the commercial muriatic acid diluted with 3 ounces (100 c. c.) of water, will yield between 3 and 4 gallons (about 15 litres) of the gas. Care must be taken not to use an acid more dilute than 1·15 in the preparation of the gas; since, owing to a neglect of this precaution,

explosions have in some instances occurred in operating on the large scale: hypochlorous acid, or one of the lower explosive oxides of chlorine, was probably formed in these cases.

2. Chlorine may also be easily obtained from a mixture of  $10\frac{1}{2}$  parts by weight of oil of vitriol, previously diluted with 7 parts of water, and allowed to cool, and 4 parts of pounded sodic chloride mixed intimately with 3 parts of finely pulverized black oxide of manganese. In this case the whole of the chlorine is expelled in the gaseous state, the sodium remaining in the form of hydro-sodic sulphate, and the manganese in that of manganous sulphate, whilst the oxygen of the oxide is separated in the form of water produced by combination with hydrogen derived from the oil of vitriol. The decomposition may be represented as follows:—



The gas comes off slowly in the cold, but freely on the application of a gentle heat. A little hydrochloric acid is always formed in the reaction; this acid is easily removed from the chlorine by allowing the gas to bubble up through a vessel containing water, in the manner shown in fig. 299, where a similar apparatus is employed for carbonic oxide.

*Uses.*—Besides the application of chlorine on the large scale, in bleaching, it is frequently employed for disinfecting purposes. In the laboratory it is in continual requisition as an oxidizing agent: owing to its attraction for hydrogen it readily decomposes water, and liberates oxygen, which at the moment that it is set free enters readily into combination. The preparation of potassic chlorate (382), of ferric acid (759), and of the sesquioxides of cobalt and nickel (720, 730), afford illustrations of this mode of employing it; and, in researches upon the nature of many products furnished by organic chemistry, it often, as in the series of compounds obtained from Dutch liquid (488), is used as a means of throwing light upon their molecular constitution.

*Chlorides.*—Chlorine combines with all the non-metals, uniting spontaneously with many of them, and forming compounds of great importance; it also enters into combination with all the metals, several of which it attacks energetically at common temperatures, exhibiting the usual phenomena of combustion; the compounds which it forms are termed *chlorides*. With the exception of argentic chloride, and mercurous and cupreous chlorides, they are all more or less soluble in water. The lower chlorides of



gold and platinum, and chloride of lead are but sparingly soluble, especially the former two. It frequently happens that chlorine combines with the same metal in more proportions than one: for example, with iron, ferrous chloride ( $\text{FeCl}_2$ ) and ferric chloride ( $\text{Fe}_2\text{Cl}_3$ ) may be formed; with platinum, platinous chloride ( $\text{PtCl}_2$ ), and platinic chloride ( $\text{PtCl}_4$ , formerly distinguished as the bi-chloride) may be obtained; and generally, for each basic oxide of the metal, a corresponding chloride exists (538).

Chlorine when in solution in the uncombined form is easily recognized by its odour and its bleaching properties. Both when free, and when combined with a metal, it gives, on the addition of a solution of argentic nitrate, a curdy, flocculent, white precipitate which changes to violet on exposure to light: this white precipitate consists of argentic chloride, and is easily re-dissolved by adding a small quantity of solution of ammonia, but it is insoluble in nitric acid even at a boiling temperature. When free chlorine acts upon argentic nitrate, a small quantity of chlorate is formed with the chloride, whilst nitric acid is liberated:  $3\text{Cl}_2 + 6\text{AgNO}_3 + 3\text{H}_2\text{O} = 5\text{AgCl} + \text{AgClO}_3 + 6\text{HNO}_3$ .

(374) HYDROCHLORIC ACID: *Muriatic acid, Hydric chloride*, ( $\text{HCl} = 36.5$ ); *Theoretic Sp. Gr.* 1.2610; *Observed*, 1.2474; *Atomic and Mol. Vol.*  $\square$ ; *Rel. wt.* 18.25.—The most important of the compounds of chlorine with the non-metals is that which it forms with hydrogen. The two gases may be mixed in equal volumes, and they will remain without action upon each other, if kept in the dark; but the moment that they are brought into direct sunlight they unite with a powerful explosion, and a colourless, intensely acid gas is the product. In diffused daylight the combination takes place gradually; but the application of a lighted match, or the passage of the electric spark through the mixture, instantly determines its explosion. One volume of chlorine unites thus with 1 volume of hydrogen, producing 2 volumes of hydrochloric acid; no condensation therefore occurs in the act of union. The composition of hydrochloric acid is consequently the following:—

			By weight.		By vol.	Sp. gr.
Chlorine	...	Cl	= 35.5	or 97.26	1 or 0.5	= 1.2265
Hydrogen	...	H	= 1.0	2.74	1	0.5 = 0.0345
Hydrochloric acid		HCl	= 36.5	100.00	2	1.0 = 1.2610

So powerful is the attraction of chlorine for hydrogen, that if either a solution of chlorine in water, or the gas itself in a moist state, be exposed to the sun's rays, water is decomposed, hydrochloric acid is formed, and the oxygen of the water is

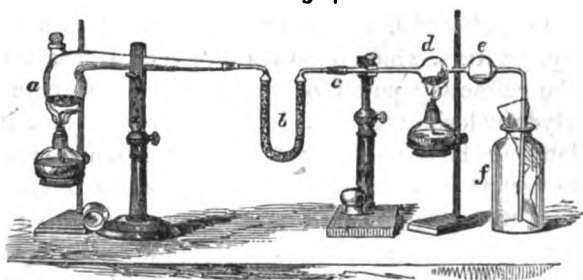
liberated: in the dark, however, chlorine has no power to decompose water.

If moist chlorine be transmitted through a red-hot porcelain tube, hydrochloric acid is formed, and oxygen is set free;  $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$ ; though, on the other hand, when hydrochloric acid gas is mixed with air and transmitted through an ignited porcelain tube, chlorine is liberated and water is produced.

The composition of hydrochloric acid may be analytically determined by heating sodium in a measured volume of the gas. The metal burns vividly, and liberates a quantity of hydrogen equal in bulk to that of half the gas employed; common salt is formed at the same time. Analogous results are obtained if iron or tin be substituted for sodium; ferrous or stannous chloride being formed, whilst hydrogen is set at liberty. As Hofmann has shown, the decomposition may also be effected without the aid of heat by agitating a given measure of dry hydrochloric acid gas with an amalgam of sodium, introduced into the gas as it stands over mercury. In a few minutes the volume is reduced to one half, and pure hydrogen is left.

The presence both of hydrogen and of chlorine in the acid gas is easily shown by the following experiment (Graham):—A quantity of hydrochloric acid is liberated from fused sodic chloride by oil of vitriol, contained in the retort, *a*, fig. 304, and

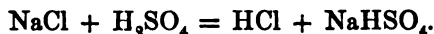
FIG. 304.



is dried by being passed through a tube, *b*, filled with calcic chloride: this tube is connected by vulcanized caoutchouc, *c*, with a tube upon which two bulbs have been blown: in the first of these, *d*, some pounded anhydrous black oxide of manganese is placed: a piece of litmus-paper inserted in the bottle, *f*, which receives the escaping gas, is quickly reddened. On applying heat to the bulb, *d*, containing the oxide, manganous chloride is produced, and as it is not volatile, it remains in the bulb, whilst water is formed and becomes condensed in the second bulb, *e*; in the

meantime free chlorine passes on into the bottle, *f*, showing itself by its peculiar colour and its bleaching effect upon the litmus-paper. The reaction has already been explained, and may be represented by the following symbols:  $4\text{HCl} + \text{MnO}_2 = 2\text{H}_2\text{O} + \text{MnCl}_2 + \text{Cl}_2$ .

*Preparation.*—Hydrochloric acid gas is easily procured by introducing fragments of common salt (which has been fused in a crucible at a red heat and allowed to cool) into a glass retort, and pouring over it twice its weight of oil of vitriol. Abundance of hydrochloric acid gas escapes; it must be collected either over mercury or by displacement of the air from dry bottles. An ounce, or 30 grms., of salt yields about 350 cubic inches (6 litres) of the gas. In this case half the hydrogen of the oil of vitriol is transferred to the chlorine of the common salt, whilst the remaining hydrogen and the sulphur combine with the sodium and form hydro-sodic sulphate, as is shown in the following equation:—



*Properties.*—Hydrochloric acid is a colourless gas, of a peculiar, pungent odour, and an intensely acid taste; it irritates the eyes, and if breathed even when largely diluted produces coughing. It is also very injurious to vegetation, causing the leaves to shrivel and turn brown. It is heavier than air; 1 litre of the gas at 0° C. and 760<sup>mm</sup>. weigh 1·6392 grm., or 100 cubic inches at 60° and 30 inches Bar. weigh 39·64 grains. Under a pressure of 40 atmospheres at 50° (10° C.) it becomes condensed to a colourless liquid of sp. gr. 1·27, which dissolves bitumen; it has never been frozen; the refracting power of this liquid is less than that of water. Hydrochloric acid gas is incombustible, and it extinguishes burning bodies. It reddens dry litmus-paper; when allowed to escape into the air it produces white fumes by condensing the atmospheric moisture, and forming with it a body less volatile than pure water. It is instantly absorbed by water: a lump of ice liquefies in a jar of the gas and absorbs it in a moment.

(375) *Solution of Hydrochloric Acid.*—The solution of hydrochloric acid in water is an indispensable requisite in the laboratory. It is easily prepared for use by placing in a capacious retort 3 parts of fused sodic chloride in fragments, and introducing gradually, through a bent funnel, 5 parts of oil of vitriol. If pounded salt be used, the action of the acid is apt to be too rapid. The retort is connected with a couple of Woulfe's bottles; in the first a small quantity of water is placed to detain any impurities which might be carried over mechanically with the gas; the second

bottle may contain 4 parts of water, and should be immersed in a vessel of cold water, as the condensation of the gas is attended with a great disengagement of heat. On applying a gentle heat to the retort the acid comes over and is condensed; the easily soluble hydro-sodic sulphate remains in the retort, as explained above. For manufacturing purposes the decomposition is effected in iron cylinders, like those employed in the preparation of nitric acid (359); only one-half the quantity of sulphuric acid prescribed above is used, and a higher temperature is applied than when glass vessels are employed;  $2\text{NaCl} + \text{H}_2\text{SO}_4 = 2\text{HCl} + \text{Na}_2\text{SO}_4$ . The sulphuric acid in this case is in the proportion of one equivalent to each equivalent of salt, normal sodic sulphate remaining in the cylinder, whilst the hydrochloric acid is condensed in a series of salt-glazed stoneware jars, arranged as Woulfe's bottles. Hydrochloric acid is produced in enormous quantities in the manufacture of salt cake (586): it is extensively employed in the arts, particularly in the preparation of chlorine as a preliminary to the manufacture of chloride of lime and potassic chlorate. It is also largely used as a solvent for tin by the dyer and calico printer, as well as in the manufacture of sal ammoniac.

Water at  $40^\circ$  ( $4.5^\circ\text{C}$ .) absorbs nearly its own weight, or about 480 times its bulk of hydrochloric acid gas, increasing in volume about one-third, and acquiring a density of 1.2109. It forms a colourless, fuming liquid, which, by a slight elevation of temperature, parts with the gas abundantly; at this strength it contains nearly 43 per cent. of acid, which is about the proportion indicated by the formula,  $\text{HCl}, 3\text{H}_2\text{O}$ .

If the strong acid be placed in a retort, and distilled, it loses hydrochloric acid, until the liquid which remains has a density of 1.100 at  $60^\circ$ ; at this point it distils unchanged. A weaker acid if distilled parts with its water freely, until it acquires the density of 1.100, and then it likewise distils unchanged, at a temperature of  $233^\circ$  ( $112^\circ\text{C}$ .). Such an acid contains about 20 per cent. of hydrochloric acid, and corresponds in composition with the formula,  $\text{HCl}, 8\text{H}_2\text{O}$ .\* Common hydrochloric acid may therefore

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\* Roscoe and Dittmar (*Q. J. Chem. Soc.* xii. 128), by varying the pressure under which the distillation is effected, have, however, shown that this apparent constancy of composition is really an accidental circumstance, and that there is no definite hydrate of this acid; but that for every pressure an aqueous solution exists, which, when distilled under that pressure, possesses a fixed composition and fixed boiling-point. For example, when distilled under a pressure of  $50^{\text{mm}}$ . of mercury, the distillate contained 23.2 per cent. of hydrochloric acid; distilled under  $380^{\text{mm}}$ . pressure, the percentage of acid was 21.3, corresponding to the formula  $2\text{HCl}, 15\text{H}_2\text{O}$ ; whilst under a pressure of  $760^{\text{mm}}$ . the per-

easily be purified by dilution till it has a sp. gr. of 1.1, and then distilling.\* Bineau, by concentration of the acid at the ordinary temperature of the air *in vacuo* over sulphuric acid, obtained a hydrate ( $\text{HCl}, 6\text{H}_2\text{O}$ ) of sp. gr. 1.128, containing 25 per cent. of the anhydrous acid. According to this observer (*Ann. de Chimie*, III. vii. 259), the vapour of the acid, sp. gr. 1.10, has a density of 0.69, 1 volume of the acid and 8 volumes of aqueous vapour being united without condensation; probably they exist in a state of mere admixture.

Commercial hydrochloric acid is liable to be contaminated with iron, which gives it a yellow colour; and with the chlorides of sodium and arsenic, the latter derived from the sulphuric acid employed in its preparation. Sulphuric and sulphurous acids and free chlorine are also often present in it. If pure, the acid should leave no residue when evaporated; on saturating it with ammonia it should give no precipitate of ferric oxide; sulphuretted hydrogen should produce no turbidity in it, which would be the case if arsenic, free chlorine, or sulphurous acid were present; and after dilution with three or four times its bulk of water, no white cloud of baric sulphate should be produced by the addition

*Strength of Hydrochloric Acid, 77° (25° C.) (E. Davy.)*

Specific gravity.	Hydrochloric acid in 100 parts.	Specific gravity.	Hydrochloric acid in 100 parts.
1.21	42.43	1.10	20.20
1.20	40.40	1.09	18.18
1.19	38.38	1.08	16.16
1.18	36.36	1.07	14.14
1.17	34.34	1.06	12.12
1.16	32.32	1.05	10.10
1.15	30.30	1.04	8.08
1.14	28.28	1.03	6.06
1.13	26.26	1.02	4.04
1.12	24.24	1.01	2.02
1.11	22.22		

of baric chloride. Traces of sulphurous acid are also easily detected by Löwenthal's test, which consists in the addition of a

centage of acid was reduced to 20.24 ( $\text{HCl}, 8\text{H}_2\text{O}$ ); if distilled under a pressure of 1520<sup>mm.</sup> or 2 atmospheres, the amount of acid fell to 19.0; and under 2280<sup>mm.</sup> or 3 atmospheres, as low as 18.2 of HCl per cent.; the composition of the liquid in the last case corresponding nearly to  $\text{HCl}, 9\text{H}_2\text{O}$ . Water at 0° C., according to these observers, dissolves 0.825 of its weight of hydrochloric acid gas, under a pressure of 760<sup>mm.</sup> of mercury; and at 15° C. it dissolves 0.745 of its weight.

\* Chlorine, however, as well as arsenious chloride and sulphurous acid, passes over with the distillate, if present.

mixture of ferric chloride and potassic ferricyanide: if sulphurous acid be present, Prussian blue is formed by the reducing action of the acid on the mixture.

The preceding table contains the amount by weight of hydrochloric acid in 100 parts of solutions of the acid of the various densities therein enumerated.

A solution of hydrochloric acid is decomposed by all the metals which decompose water at a red heat: the metal is dissolved, and hydrogen gas is set free, just as when iron or zinc is acted upon by diluted sulphuric acid: for example,  $2\text{HCl} + \text{Zn} = \text{ZnCl}_2 + \text{H}_2$ .

(376) *Action of Hydrochloric Acid on Metallic Oxides.*—The action of hydrochloric acid upon the oxides of the metals is important. Protoxides are dissolved by the acid, and appear to combine with it; but on evaporating the liquid, a saline compound is obtained in which neither hydrochloric acid nor the metallic oxide is present, and which contains neither hydrogen nor oxygen; double decomposition ensues. When the hydrated oxide of a monad metal, such as sodic hydrate, combines with hydrochloric acid, the hydrogen of the acid changes places with the metal, and is exactly sufficient with the residue, HO, of the hydrate to form water, which remains in the solution, or else evaporates on the application of heat, whilst the metal and the chlorine unite directly with each other, as is shown by the following symbols;  $\text{NaHO} + \text{HCl}$  yield  $\text{NaCl} + \text{H}_2\text{O}$ .

When the anhydrous oxide of either a monad or a dyad is employed, the reaction is similar, but two atoms of hydrochloric acid are concerned, and the metal exchanges places with two atoms of hydrogen:—



But though the metal may exist in solution in the form of chloride, this circumstance does not prevent its precipitation as oxide, when a strong base, such as potassic hydrate, is added to a solution which contains the chloride of the metal in question, provided that the metal be capable of forming an oxide insoluble in water. For example, if to a solution of cupric chloride a solution of potassic hydrate be added, the potassium and copper change places, potassic chloride is formed and dissolved, whilst cupric hydrate is precipitated. It is, in fact, an ordinary instance of double decomposition:—



A reaction not less instructive occurs when oxides containing a larger proportion of oxygen than the protoxides are treated with hydrochloric acid. When, for instance, 1 atom of ferric oxide ( $\text{Fe}_2\text{O}_3$ ) is subjected to its influence, 6 atoms of hydrochloric acid are decomposed, 3 atoms of water are formed, and an atom of ferric chloride is obtained in solution :—



It sometimes happens that no chloride corresponding to the oxide exists. There is, for example, no stable tetrachloride of manganese : in this case 1 atom of manganic dioxide ( $\text{MnO}_2$ ) decomposes 4 atoms of hydrochloric acid ; 2 atoms of water and 1 atom of manganous chloride are formed, whilst 2 atoms of chlorine are liberated ; this being, in fact, the usual mode of obtaining chlorine gas :



The presence of hydrochloric acid and of the soluble chlorides in solution is indicated by the formation of a white, insoluble, curdy precipitate of argentic chloride, when a solution of argentic nitrate is added to the liquid ;  $\text{NaCl} + \text{AgNO}_3$  becoming  $\text{AgCl} + \text{NaNO}_3$ . This precipitate is soluble in ammonia, but insoluble in nitric acid, even when boiling, though soluble in solution of sodic hyposulphite, and of potassic cyanide. Mercurous nitrate also gives a white precipitate of mercurous chloride (calomel) in solutions of metallic chlorides :  $\text{HgNO}_3 + \text{NaCl} = \text{NaNO}_3 + \text{HgCl}$ . The precipitate is soluble in chlorine water, insoluble in diluted nitric acid, and is immediately blackened by ammonia. The dry chlorides when heated with potassic dichromate and sulphuric acid yield a red liquid ( $\text{CrO}_2\text{Cl}_2$ ), which forms a yellow solution with ammonia : this reaction distinguishes the chlorides from the bromides.

(377) *AQUA REGIA : Nitro-muriatic acid.*—The name of *aqua regia* was given by the alchemists to a mixture of nitric with hydrochloric acid, from the power that it possesses of dissolving gold, the ‘king of metals.’ Both platinum and gold are insoluble in either acid separately ; but when the two acids are mixed, they decompose each other ; free chlorine, and abundant ruddy fumes, long mistaken for peroxide of nitrogen, being liberated : the chlorine in the moment of its extrication acts upon the metals and dissolves them. (Gay-Lussac ; *Ann. de Chimie*, III. xxiii. 203.)

*Nitric Oxydichloride*, or *Chloro-nitric gas* ( $\text{NOCl}_2$ ) ; *Boiling-point*,  $19^\circ$  ( $-7^\circ \text{C.}$ ).—If a mixture of 1 part of concentrated nitric acid and 3 parts of hydrochloric acid be placed in a flask and subjected to a gentle heat in the water bath, red fumes pass off in abundance. These vapours, if transmitted through a bottle cooled by immersion in melting ice, deposit a little volatilized hydrochloric acid and water, but the red fumes pass on, and may be condensed

as a heavy red liquid, in a tube receiver which is plunged into a mixture of ice and salt, while free chlorine escapes from the open extremity of the tube. In this reaction 2 atoms of nitric acid decompose 6 of hydrochloric acid, producing 2 of the red compound ( $\text{NOCl}_2$ ), 4 atoms of water, and 2 of free chlorine;  $2\text{HNO}_3 + 6\text{HCl}$  yielding  $2\text{NOCl}_2 + 4\text{H}_2\text{O} + \text{Cl}_2$ .

Nitric oxydichloride may be regarded as peroxide of nitrogen, in which 2 atoms of chlorine have taken the place of 1 atom of oxygen. At all temperatures above  $19^\circ$  ( $-7^\circ \text{C.}$ ), it is a gas of a deep lemon-yellow colour, with the suffocating odour of aqua regia. It may be condensed by transmitting it through a tube surrounded by a freezing mixture of ice and salt, when it forms a transparent, red, fuming liquid. Water decomposes the compound immediately, appearing to dissolve it: but the solution contains hydrochloric acid and the elements of peroxide of nitrogen;  $\text{NOCl}_2 + \text{H}_2\text{O}$  give  $\text{NO}_2 + 2\text{HCl}$ .

A similar decomposition ensues when it is mixed with an alkaline base, for it does not form salts. The gas cannot be confined over mercury, since it attacks the metal instantly, forming calomel and liberating nitric oxide;  $\text{NOCl}_2 + 2\text{Hg}$  giving  $2\text{HgCl} + \text{NO}$ .

*Nitrous Oxychloride*, or *Chloro-nitrous gas* ( $\text{NOCl}$ ); *Theoretic Sp. Gr.* 2.265; *Atomic Vol.*  $\square$ ; *Rel. wt.* 32.75.—When chlorine is mixed with nitric oxide in the gaseous state, they combine and yield a dense orange-coloured gas; 2 volumes of nitric oxide and 1 of chlorine produce 2 volumes of the new compound. It cannot be formed over mercury, as it is immediately decomposed by this metal. At a temperature of  $0^\circ$  ( $-18^\circ \text{C.}$ ) it is reduced to a red liquid resembling the chloro-nitric compound in odour and aspect, and which boils at about  $32^\circ$  ( $0^\circ \text{C.}$ ).

Aqua regia, under certain circumstances, may produce both chloro-nitric and chloro-nitrous gas, just as the nitric oxide may, according to the circumstances under which it is mixed with oxygen, form either nitrous anhydride, or peroxide of nitrogen. In the early stages of the decomposition of aqua regia, the product is nearly pure nitric oxydichloride ( $\text{NOCl}_2$ ), but as the decomposition advances, the quantity of nitrous oxychloride ( $\text{NOCl}$ ) increases. Neither of these chlorinated compounds exerts any solvent action upon gold or platinum.

By the action of dry hydrochloric acid gas upon anhydrous peroxide of nitrogen, a third chlorinated compound,  $\text{NO}_2\text{Cl}$ , *nitric chlorodioxide* (*sp. gr. of liquid* 1.32; *of vapour* 2.63; *rel. wt.* 40.75), appears to be formed, mixed with other bodies.

Aqua regia is largely employed as an oxidizing agent; by its action perchlorides of the metals are formed in solution, and when the liquid is decomposed by an alkali, the oxide of the metal corresponding in composition to its perchloride is precipitated. By boiling the solutions of the metals in aqua regia with an excess of hydrochloric acid, the whole of the nitric acid may be decomposed and expelled, and a pure solution of the metallic chlorides with excess of hydrochloric acid will be formed.

(378) OXIDES OF CHLORINE.—The attraction of chlorine for



oxygen is so feeble that the two elements do not enter directly into combination with each other. Several compounds of oxygen and chlorine may, however, be obtained by indirect methods. Three of these oxides may be obtained in the isolated form; they are the following :—

		Mol. vol.	In 100 parts.	
			Cl.	O.
Hypochlorous anhydride ...	$\text{Cl}_2\text{O} =$	87	18'60	+ 18'40
Chlorous anhydride ...	$\text{Cl}_2\text{O}_3 =$	119	59'66	+ 40'34
Chloric peroxide, or dioxide	$\text{ClO}_2 =$	67'5	52'59	+ 47'41

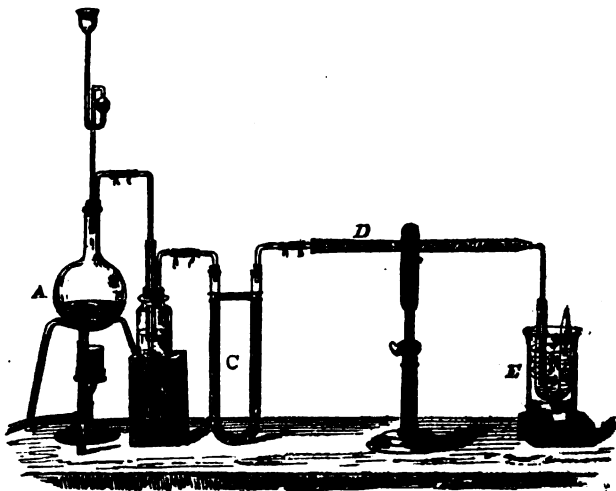
Four monobasic oxidized acids of chlorine may also be obtained, viz. :—

Hypochlorous acid ...	...	...	$\text{HClO} =$	52'5
Chlorous acid ...	...	...	$\text{HClO}_2 =$	68'5
Chloric acid ...	...	...	$\text{HClO}_3 =$	84'5
Perchloric acid ...	...	...	$\text{HClO}_4 =$	100'5

Millon's experiments have rendered it probable that other oxidized compounds also exist, the result of the combination of some of those already mentioned with chloric and perchloric anhydrides.

(379) **HYPOCHLOROUS ANHYDRIDE** ( $\text{Cl}_2\text{O}=87$ ); *Mol. Vol.* ; *Rel. wt.* 43'5; *Theoretic Sp. Gr.* 3'005; *Boiling-pt.* about 68° (20° C.).—If chlorine in a perfectly dry state be passed slowly through a tube, D, fig. 305, filled with well-dried mercuric oxide,

FIG. 305.



obtained by precipitation from a solution of corrosive sublimate by means of caustic potash, immediate action commences, and a gas is produced which may be condensed into a liquid by sur-

rounding the tube receiver, *E*, with a mixture of ice and salt. The chlorine is prepared in the flask, *A*, washed with water in the bottle, *B*, and dried by allowing it to traverse the bent tube, *C*, which is filled with pumice-stone moistened with oil of vitriol.

The reaction between the chlorine and mercuric oxide appears to be of a simple nature: 2 atoms of chlorine displace 1 atom of oxygen from the mercury, and this oxygen at the moment of its liberation unites with two other atoms of chlorine to form hypochlorous anhydride;  $\text{HgO} + 2\text{Cl}_2 = \text{HgCl}_2 + \text{Cl}_2\text{O}$ . Hypochlorous anhydride is thus procured as a deep red liquid, which emits a vapour of a deeper colour than that of chlorine, with a peculiar suffocating chlorous smell. This vapour is remarkable for the ease with which it is decomposed, the warmth of the hand causing its separation into chlorine and oxygen with explosion; 2 volumes of the anhydride in this way produce a mixture composed of 2 volumes of chlorine and 1 volume of oxygen. The composition of the gas is therefore as follows:—

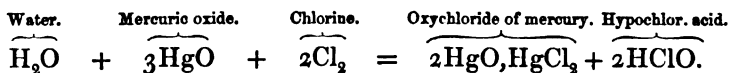
			By weight.		By volume.		Sp. gr.
Chlorine	...	$\text{Cl}_2$	=	71 or 81·6	2 or 1·0	=	2·453
Oxygen	...	$\text{O}$	=	16 18·4	1 0·5	=	0·552
		<hr/>		<hr/>	<hr/>		<hr/>
Hypochlorous	}	$\text{Cl}_2\text{O}$	=	87 100·0	2 1·0	=	3·005
anhydride							

*Hypochlorous acid; Hydric hypochlorite;  $\text{HClO} = 52·5$ .—* Water dissolves about 200 times its bulk of gaseous hypochlorous anhydride, and forms with it a pale yellow solution, which has an acrid, but not sour taste;  $\text{Cl}_2\text{O} + \text{H}_2\text{O} = 2\text{HClO}$ . In a concentrated form this solution is very unstable; it acts as a powerful oxidizing agent; but is rapidly decomposed when exposed to the light, bubbles of chlorine escaping from it, whilst chloric acid is formed. Charcoal, iodine, sulphur, selenium, phosphorus, arsenicum, and finely powdered antimony, decompose a solution of hypochlorous acid rapidly, and are converted by it respectively into carbonic, iodic, sulphuric, selenic, phosphoric, arsenic, and antimonie acids: if the solution be concentrated the action is sometimes attended with explosion. Iron filings are also immediately oxidized with evolution of chlorine. Silver is converted into chloride whilst oxygen is liberated, and copper and mercury combine with both the oxygen and the chlorine, furnishing oxychlorides. The contact of argentic chloride with the solution of the acid also decomposes the latter, causing the separation of both oxygen and chlorine in the gaseous form, whilst the metallic chloride appears to have undergone no alteration. Hypochlorous acid attacks the skin and turns it brown; but its most important

property is its bleaching power, which, according to the experiments of Gay-Lussac, is twice as great as that of the chlorine which it contains. When hypochlorous acid or any of its salts is heated with hydrochloric acid in excess, an atom of each acid is decomposed, water is formed, and 2 atoms of chlorine are liberated;  $\text{HCl} + \text{HClO} = \text{H}_2\text{O} + \text{Cl}_2$ . If a fragment of sal ammoniac be suspended in a solution of hypochlorous acid, oily-looking drops of the explosive compound known as chloride of nitrogen (386) are formed.

Hypochlorous acid by its action upon the alkalies and earths, furnishes salts termed *hypochlorites*. These compounds are decomposed even by feeble acids, such as the carbonic; and the hypochlorous acid thus liberated, shows its usual bleaching action on vegetable colours. The solutions of these salts are decomposed by gently heating them, and they become converted into a mixture of chloride and chlorate;  $3\text{KClO}$  becoming  $2\text{KCl} + \text{KClO}_3$ . This change is retarded by the addition of an excess of caustic alkali.

When chlorine acts upon the oxides of metals which have but a feeble attraction for oxygen, these bases are often completely decomposed. In consequence of this reaction, a weak solution of hypochlorous acid is easily prepared by agitating 1 part of the red oxide of mercury with 12 parts of water in a large bottle of chlorine gas, care being taken that the mercuric oxide is in slight excess. The chlorine is rapidly absorbed; part of the oxide of mercury is decomposed by the chlorine, and the mercuric chloride thus produced unites with a portion of unchanged mercuric oxide, forming a brown insoluble oxychloride of that metal; the solution on being decanted is found to contain hypochlorous acid. The reaction may be represented as follows:—

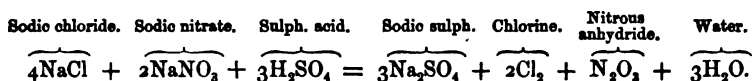


(380) *Bleaching Compounds*.—If the base upon which chlorine is made to act, be a powerful one, such as an alkali or alkaline earth, the gas is absorbed, and a peculiar compound possessed of bleaching properties is produced. It is in this way that the bleaching compounds so extensively used in the arts under the names of chloride of lime, chloride of potash, and chloride of soda, are prepared.

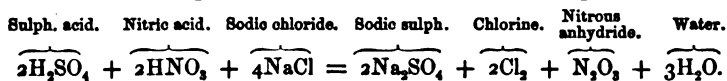
Of these bleaching compounds the chloride of lime is the most important. It is prepared by slaking well-burnt lime, and exposing it to the action of chlorine gas in layers of 5 or 8 centim.

(2 or 3 inches) in thickness, upon perforated shelves in chambers made of lead, or of Yorkshire flagstones. The chlorine must be admitted gradually, in order to prevent too rapid a rise of temperature consequent upon a quick absorption of the gas. If the heat be allowed to rise much beyond  $100^{\circ}$  ( $38^{\circ}$  C.), a quantity of calcic chloride and chlorate is formed, the reaction being similar to that which occurs during the preparation of potassic chlorate (382). Slaked lime ( $\text{CaH}_2\text{O}_2$ ) may in this operation be made to take up about half its weight of chlorine; but it is not possible to combine calcic hydrate in the form of powder with an entire equivalent of chlorine so as to form the compound  $\text{CaOCl}_2$ : the product always contains a considerable excess of uncombined lime.

A few years ago, Mr. Dunlop, of the St. Rollox Works, Glasgow, introduced a method of preparing chlorine for the manufacture of bleaching powder, by decomposing a mixture of common salt and sodic nitrate with sulphuric acid. In this operation chlorine and nitrous anhydride are evolved, whilst sodic sulphate is produced; the reaction may be traced by the equations following:—

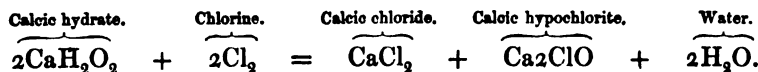


The mixed gases are made to pass through a vessel containing oil of vitriol, by which the nitrous anhydride is rapidly absorbed, whilst the chlorine passes on to the lime. A current of air is made to act on the nitrous sulphuric acid, by which the nitrous acid becomes converted into nitric acid, owing to the absorption of oxygen; and the mixed acids being made to act upon fresh sodic chloride, without the addition of nitre, give rise to a similar succession of decompositions:—



The nitrous sulphuric acid may also be at once made use of in the leaden chambers in the manufacture of oil of vitriol (413).

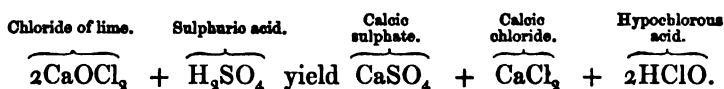
Many chemists consider both chloride of lime and the corresponding compounds with potash and soda to be hypochlorites of the metals which enter into their formation: in this case they must be double salts of the hypochlorite and chloride of the metal. This, however, is more than questionable; they are probably direct combinations of chlorine with the oxides. If the compound be supposed to be a pure chloride of lime or calcic oxydichloride, the reaction is simply an absorption of chlorine, by which the compound  $\text{CaOCl}_2$  is formed; but if it be supposed that a hypochlorite is produced, the following decomposition must occur:—



Calcic chloride is deliquescent, and is soluble in alcohol; but

bleaching powder, when properly made, is not deliquescent, and yields scarcely any calcic chloride to alcohol.

Chloride of lime emits the peculiar odour of hypochlorous acid when exposed to the air; under these circumstances, however, it gradually absorbs carbonic anhydride, and exhales, not hypochlorous acid, but chlorine,—a circumstance which causes it to be extensively used as a disinfecting agent. Cloths dipped in an aqueous solution of the chloride, when hung up in the room to be fumigated, continue for many hours to emit chlorine gradually, but in quantities too small to be injurious to the inmates. Commercial chloride of lime is only partially soluble in water, and leaves a large residue of calcic hydrate. An excess of any acid when poured upon the powder causes a free evolution of chlorine; but if the aqueous solution be mixed with half the quantity of sulphuric acid required to neutralize the lime, hypochlorous acid may be distilled off and condensed in a diluted form in a suitable receiver. The reaction which occurs may be thus represented:—



Chloride of lime is consumed in vast quantities in the bleaching of calicoes and other woven goods. The calico is well washed, and boiled successively with lime-water, with much diluted sulphuric acid, and with a weak solution of caustic soda, in order to remove the weaver's dressing, and greasy and resinous matters: it is then well washed, and digested in a solution of chloride of lime, containing 2 or  $2\frac{1}{2}$  per cent. of bleaching powder. The bleaching effect of this solution is not, however, rendered apparent till the goods are immersed in very dilute sulphuric acid, which decomposes the chloride of lime immediately, and by liberating chlorine within the fibres of the cloth itself, rapidly removes the colour. Still, however, it is not perfectly white. The calico is therefore washed, and a second time subjected to the action of caustic alkali, to remove the colouring matter now rendered soluble in it by the action of the chlorine: again it is passed through a weaker solution of chloride of lime, and then through dilute acid; finally it is thoroughly washed in a copious stream of water, in order to remove the last traces of sulphuric acid, which would otherwise destroy the fibre.

(381) *Estimation of the Bleaching Power of Chloride of Lime.*—

The commercial value of bleaching powder depends upon the quantity of chlorine which can be liberated from it by the addition of an acid; for it is this portion of its chlorine only which is available for bleaching purposes. Gay-Lussac proposed to estimate the bleaching power by measurement of the bulk of a solution

of indigo of known strength which a given weight of the chloride is able to deprive of its blue colour; and subsequently he determined the amount of available chlorine by the quantity of a standard solution of arsenious acid which could be converted by a known weight of the bleaching powder into arsenic acid.

A still more convenient plan has been described by Graham. It depends upon the determination of the quantity of a ferrous salt which a given weight of bleaching powder in the presence of an excess of acid can convert into a ferric salt: if ferrous sulphate be used, 2 atoms of chlorine are required for the conversion of 2 atoms of that salt into 1 atom of ferric sulphate; the chlorine decomposing water and becoming hydrochloric acid, as is shown in the following equation:—

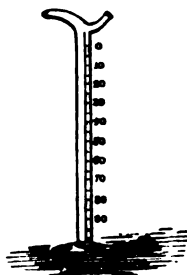


7·8 grammes of crystallized ferrous sulphate require 1 gramme of chlorine for its conversion into the ferric sulphate. In making an experiment upon the value of a bleaching powder, 7·8 grms. of clean dry crystals of the green sulphate are dissolved in about 60 cub. centim. of water, and acidulated with sulphuric or hydrochloric acid; 5 grms. of the bleaching powder are rubbed up in a mortar with 60 cub. centim. of warm water, and transferred to a burette or tall narrow tube (fig. 306), capable of holding 100 cub. centim. of water, and graduated into 100 equal parts from above downwards. The mortar is washed with a little more water, and the washings added to the liquid in the burette, which is filled up exactly to 0°. The openings at top are closed with the finger and thumb, and the contents of the vessel are mixed thoroughly by agitation. The solution of chloride of lime is then added gradually to the ferrous sulphate (constantly stirring the mixture), until the whole of the ferrous salt is converted into ferric salt. The progress of the oxidation is ascertained by means of a solution of the red prussiate of potash, or potassic ferricyanide ( $\text{K}_3\text{FeCy}_6$ ), which strikes a deep blue with the liquid if it contain any unchanged ferrous sulphate. Several drops of the ferricyanide are spotted over a white plate, and, after each addition of the chloride of lime to the solution of sulphate, a drop of the iron solution is mixed with one of these, and the addition of the chloride is continued so long as the blue colour appears. The stronger the bleaching powder, the fewer will be the number of divisions required to be poured from the burette. This number of divisions divided by 2 will indicate the number of grms. of bleaching powder which contain 1 gramme of available chlorine. The strength of the powder is therefore obtained by the following proportion, in which  $m$  represents the number of measures poured from the burette:—

$$\frac{m}{2} : 1 :: 10 : x \text{ (the number of grms. of chlorine in 10 grms. of the powder);}$$

$$\text{or } \frac{20}{m} = x.$$

FIG. 306.

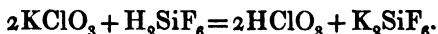


The process of converting a lower oxide of a metal into one of its higher oxides, by means of chloride of lime, admits of being frequently employed; indeed, a solution of chloride of lime, when mixed with hydrochloric acid, furnishes a powerful oxidizing agent. Peroxide of bismuth, of cobalt, of nickel, and of lead, may be obtained readily by adding a neutral solution of chloride of lime to neutral solutions of the salts of these metals and heating the liquid.

(382) **CHLORIC ACID**; *Hydric chlorate* ( $\text{HClO}_3 = 84.5$ ).—Chloric anhydride has not been isolated, but the corresponding acid is known. If a current of chlorine gas be caused to pass through a solution of caustic potash (1 part of caustic potash and 3 parts of water), it is rapidly absorbed, even when transmitted in a continuous stream, and a bleaching liquid is formed, which, on the application of heat, loses its bleaching properties, and is gradually converted into a mixture of potassic chloride and chlorate; 6 atoms of chlorine and 6 of potassic hydrate furnishing 5 of potassic chloride and 1 atom of the chlorate, whilst water is liberated—



The potassic chlorate being sparingly soluble is freed from the chloride by two or three crystallizations. In order to obtain chloric acid, the chlorate is decomposed by the addition of hydrofluosilicic acid, which forms an insoluble compound with the potassium, and chloric acid is liberated—



The acid solution may be poured off from the precipitate, and concentrated by evaporation over the water-bath at a heat not exceeding  $100^\circ$  ( $38^\circ \text{C.}$ ), till it forms a syrupy liquid of a faint chlorous smell, and a powerfully acid taste. It is instantly decomposed by contact with organic matter, and in its concentrated form it chars and even sets fire to paper. By a temperature a little above  $100^\circ$  ( $38^\circ \text{C.}$ ) the acid is decomposed into oxygen gas, chlorine, perchloric acid, and water;  $8\text{HClO}_3$  yielding  $4\text{HClO}_4 + 2\text{H}_2\text{O} + 3\text{O}_2 + 2\text{Cl}_2$ . In diffused daylight, it gradually undergoes spontaneous decomposition. On one occasion a small specimen which I had sealed up in a glass tube was placed aside upon a shelf; but in a few weeks, although left untouched, the tube exploded in consequence of the expansive force of the liberated gases.

The metallic salts of chloric acid require a higher temperature for their decomposition than the acid itself. The action of heat upon potassic chlorate has already been mentioned as affording a very convenient source of pure oxygen (335). This salt, when heated to a point a little short of redness, fuses, and is converted ultimately into potassic chloride and oxygen gas;  $2\text{KClO}_3$  becoming  $2\text{KCl} + 3\text{O}_2$ .

This decomposition also furnishes data for ascertaining the composition of chloric acid; for if a given weight of the chlorate be calcined with suitable precaution, the loss indicates the entire quantity of oxygen which it contained. The proportions of chlo-

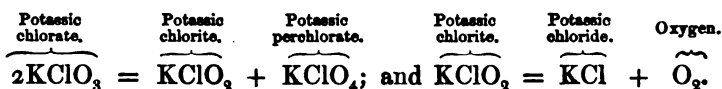
rine and of potassium in potassic chloride being known, the composition of chloric acid is readily calculated.

*Chlorates.*—The salts of chloric acid, or the *chlorates*, are monobasic, with the general formula  $M'ClO_3$ . All of them are decomposed by heat; oxygen is expelled, and generally a chloride of the metal is left behind: the chloride can be detected in the residue by argentic nitrate. The chlorates produce scintillation when thrown upon ignited charcoal; and when heated with combustible substances, such as phosphorus or sulphur, they explode violently. It generally happens that mere friction with these bodies is sufficient to cause a powerful detonation: for example, if half a grain (30 or 40 mgrms.) of sulphur be triturated in a mortar with 3 grains (2 decigrammes) of potassic chlorate, the friction is attended with a series of small explosions. A mixture which detonates powerfully when struck or rubbed may be obtained by powdering separately equal parts of antimonious sulphide ( $Sb_2S_3$ ) and potassic chlorate, then mixing them cautiously on a card with a feather. When a fragment of a chlorate is placed in a drop of oil of vitriol, a yellow colour is produced, and the peculiar odour of chloric peroxide ( $ClO_2$ ) is evolved. Nitric acid decomposes the chlorates with formation of a nitrate and perchlorate of the metal, while free chlorine and oxygen escape;  $8KClO_3 + 4HNO_3 = 4KClO_4 + 2Cl_2 + 3O_2 + 2H_2O + 4KNO_3$ . Hydrochloric acid liberates euchlorine (p. 140). Many of the chlorates are deliquescent; they are all soluble in water; but mercurous chlorate is least so: their solutions are not precipitated by argentic nitrate; many of them also are soluble in alcohol. Paper soaked in a solution of a chlorate, and allowed to dry, acquires the property of smouldering when kindled, and burns in the same manner as touch-paper. The chlorates when in solution, even in small quantity, may readily be distinguished from the nitrates, by adding first a few drops of a solution of indigo, and then a solution of sulphurous acid: the blue colour immediately disappears even without the application of heat, but it remains unaltered when nitrates only are present. The chlorates of potassium, sodium, and silver are anhydrous; that of barium contains 1 atom of water, and that of strontium 6 atoms of water.

Potassic chlorate, when in solution, often affords a convenient method of converting the metallic protoxides into peroxides; since by the addition of hydrochloric acid to the solution, chloric acid is set at liberty, and exerts its oxidizing power. Iron, for example, when it exists in a solution as a ferrous salt, is thus readily converted into a ferric salt when the liquid is boiled.



(383) PERCHLORIC ACID; *Hydric perchlorate*;  $\text{HClO}_4 = 100.5$ ; *Sp. gr. of liquid*, 1.782.—Perchloric anhydride is unknown. If instead of heating potassic chlorate to complete decomposition, the temperature be moderated and the process stopped when one-third of the total quantity of oxygen has been expelled, the mass will have assumed a pasty condition, and will be found to contain a compound of chlorine with a still higher proportion of oxygen, to which the name of perchloric acid has been given; this compound remains in combination with a portion of the potassium. The reaction appears to consist in the resolution of 2 atoms of the chlorate into 1 atom of perchlorate ( $\text{KClO}_4$ ) and 1 of chlorite of potassium ( $\text{KClO}_2$ ); the latter salt being unable to exist at so high a temperature, is immediately converted into oxygen gas and potassic chloride, as follows :—



By crystallization potassic perchlorate is readily separated from the more soluble chloride. The perchlorate is freely dissolved by boiling water, but as the salt is much less soluble at ordinary temperatures, it crystallizes from the solution as it cools, and is deposited in octohedra. At a red heat the perchlorate is itself resolved into oxygen and potassic chloride.

One method of obtaining perchloric acid in the form of hydrate consists in distilling potassic perchlorate with four times its weight of oil of vitriol: if the receiver be kept cool, the first portions that distil over crystallize in long silky deliquescent needles consisting of ( $\text{HClO}_4, \text{H}_2\text{O}$ ): a large proportion of the acid, however, is decomposed into chlorine and oxygen gases. According to Roscoe, the best method of preparing perchloric acid consists in boiling down a solution of chloric acid obtained by the action of hydrofluosilicic acid upon potassic chlorate. Lower oxides of chlorine escape, and an impure solution of perchloric acid is left, which is purified by distillation, when a heavy, colourless, thick oily liquid passes over. If this be heated it gives off dense white fumes. By distilling this liquid with four times its volume of oil of vitriol, a yellow mobile fluid consisting of pure perchloric acid ( $\text{HClO}_4$ ) first comes over. This is followed by a thick oily liquid, which is a hydrate (containing 65.8 per cent. of the anhydride), of the form ( $\text{HClO}_4, 2\text{H}_2\text{O}$ ). If this be mixed with the pure acid  $\text{HClO}_4$  in equivalent proportions, it forms the white fusible crystalline substance ( $\text{HClO}_4, \text{H}_2\text{O}$ ) already

\* During the decomposition of the chlorate a considerable evolution of heat occurs; this may be rendered manifest by projecting into the melted salt which is evolving oxygen, a little oxide of copper or ferric oxide. Although neither of these compounds is oxidized in the process, they increase the rapidity of extrication of oxygen; and the temperature of the mass rises to redness (1008), 1 part of the salt during its decomposition evolving 39 units of heat (129, 203), the combination of chlorine with potassium evolving more heat than is required for the liberation of the oxygen in the gaseous form,

described. This crystallizable hydrate when heated to  $230^{\circ}$  ( $110^{\circ}$  C.) is decomposed into the pure acid ( $\text{HClO}_4$ ) which distils over, whilst the oily hydrate remains in the retort, and does not come over till the temperature is raised to  $397^{\circ}$  ( $203^{\circ}$  C.).

Perchloric acid is a colourless volatile liquid, which soon becomes yellow owing to liberation of one of the oxides of chlorine. It remains liquid at a temperature of  $-31^{\circ}$  ( $-35^{\circ}$  C.). It is one of the most powerful oxidizing agents known; a drop of it brought into contact with charcoal, with paper, or almost any organic substance, immediately produces combustion with an explosive violence falling but little short of that of the so-called chloride of nitrogen. It produces frightful burns if allowed to fall upon the skin. It cannot be redistilled without experiencing decomposition, generally attended with explosion. If sealed up in tubes it gradually undergoes spontaneous decomposition, and the tubes burst with explosion. With water it combines with evolution of great heat, and if the proportion of water be not too large it reproduces the white crystals of Serullas ( $\text{HClO}_4 \cdot \text{H}_2\text{O}$ ). Diluted perchloric acid is of a purely sour taste, and does not destroy vegetable colours; in this form, indeed, it is the most stable of all the oxides of chlorine. It will even dissolve iron and zinc with evolution of hydrogen gas.

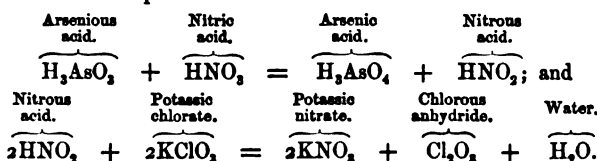
Perchloric acid forms the salts known as *perchlorates*, with the general formula  $\text{M}'\text{ClO}_4$ : they in general are deliquescent. None of them are insoluble, though potassic perchlorate requires upwards of 150 times its weight of cold water for solution; the salts of this acid with sodium, barium, and silver, are soluble in alcohol. All the perchlorates are decomposed by heat, with evolution of oxygen and formation of a chloride, but they may be distinguished from the chlorates by not yielding a yellow gas when moistened with oil of vitriol.

(384) CHLOROUS ANHYDRIDE ( $\text{Cl}_2\text{O}$ , = 119); *Sp. Gr.* 2.646; *Mol. Vol.*   ; *Rel. wt.* 39.7.—This substance may be obtained in the form of a gas of a deep yellowish-green colour; it is not liquefied by exposure to a temperature of  $-4^{\circ}$  ( $-20^{\circ}$  C.). Chlorous anhydride is a dangerous compound to prepare, as exposure to a temperature not much exceeding  $131^{\circ}$  ( $55^{\circ}$  C.) is sufficient to decompose it with a powerful explosion. Contact with most combustible non-metallic elements, such as sulphur, selenium, tellurium, and phosphorus, decomposes the gas with explosion; arsenicum has a similar effect. Most of the metals—including copper, lead, tin, zinc, and iron—are without action upon it, but mercury absorbs it completely. The gas, when dissolved in water, furnishes chlorous acid ( $\text{HClO}_2$ ); and the solution oxidizes all these metals; they commonly yield a mixture of chlorate and chloride, especially if the acid be in excess; for instance,  $2\text{Zn} + 4\text{HClO}_2 = \text{ZnCl}_2 + \text{Zn}_2\text{ClO}_3 + 2\text{H}_2\text{O}$ .

The composition of chlorous anhydride is the following, and its combining volume is anomalous, as appears from the experiments of Millon, confirmed by those of Schiel, the molecule occupying 3 volumes instead of 2:—

	By weight.	Millon.	By vol.	Sp. gr.
Chlorine	$\text{Cl}_2 = 71$ or $59\cdot66$	$60\cdot15$	$2$ or $0\cdot66$	$1\cdot635$
Oxygen	$\text{O}_2 = 48$ or $40\cdot34$	$39\cdot85$	$3$ or $1\cdot00$	$1\cdot105$
Chlorous anhydride	$\text{Cl}_2\text{O}_3 = 119$ or $100\cdot00$	$100\cdot00$	$3$ or $1\cdot00$	$2\cdot740$

This gas is soluble in about one-sixth of its bulk of water, and the solution, even when diluted very largely, has a bright yellow colour. The compound is prepared by deoxidizing chloric acid; this object is effected by means of arsenious acid, when the gas is required in a state of purity. Three parts of arsenious anhydride (white arsenic) and 4 of potassic chlorate are rubbed up into a paste with water, and 16 parts of pure nitric acid, of sp. gr.  $1\cdot24$ , are added; the whole is placed in a small flask, which is filled up to the neck with the mixture, and a very gentle heat is applied by means of a water-bath (Millon, *Ann. de Chimie*, III. vii. 322). The gas must be collected by displacement in dry bottles, as it is rapidly decomposed by mercury. In this operation the arsenious acid becomes oxidized at the expense of the nitric acid; nitrous acid is formed, and this in turn is reconverted into nitric acid by decomposing the liberated chloric acid: for example—



Tartaric acid may be substituted for arsenious anhydride in this operation, but the gas is then mixed with carbonic anhydride.

*Chlorous acid* ( $\text{HClO}_2 = 68\cdot5$ ) possesses considerable bleaching power; it acts slowly upon bases, and forms monobasic salts, termed *chlorites*, with the general formula  $\text{M}'\text{ClO}_2$ . Potassic chlorite ( $\text{KClO}_2$ ) is deliquescent: if its solution be slowly evaporated to dryness, it is converted into a mixture of chloride and chlorate of the metal, in equivalent proportions. The chlorites of sodium, barium, and strontium are also deliquescent. The chlorites are decomposed by the feeblest acids, such even as carbonic acid. Plumbic nitrate produces a sulphur-yellow scaly precipitate in their solutions, owing to the formation of plumbic chlorite ( $\text{Pb}_2\text{ClO}_3$ ). Argentic chlorite is also yellowish and insoluble.

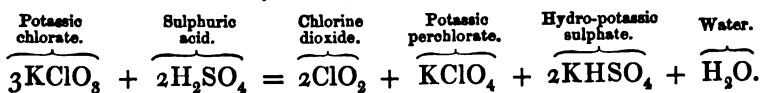
The chlorites may be distinguished from the hypochlorites by the addition of a mixture of arsenious anhydride with nitric acid, which does not destroy the bleaching power of the chlorites, whilst it destroys that of the hypochlorites. Their solutions deoxidize an acidulated solution of potassic permanganate.

(385) PEROXIDE OF CHLORINE: *Chloric Dioxide* ( $\text{ClO}_2 = 67\cdot5$ ); *Rel. wt.*  $33\cdot75$ ; *Theoretic Sp. Gr.*  $2\cdot331$ ; *Observed*,  $2\cdot3227$ ; *Boiling-pt.*  $68^\circ$  ( $20^\circ \text{C.}$ ); *Mol. Vol.*  $\square$ —This compound is gaseous at ordinary temperatures, but by slight pressure, or by exposure to a cold of  $-4^\circ$  ( $-20^\circ \text{C.}$ ), it is reducible to a red liquid, which, according to Millon, is liable to explode as powerfully as chloride of nitrogen. The gas is of a colour still deeper than that of chlorous anhydride, and has a similar but less irritating odour. It may be preserved unaltered in the dark, but is gradually decomposed in the sunlight into its component gases. Water dissolves about 20 times its bulk of the gas, and forms a yellow solution, which

bleaches powerfully. The gas requires great care in its preparation, as a temperature a little above  $140^{\circ}$  ( $60^{\circ}$  C.) or  $145^{\circ}$  determines its explosion; 2 volumes of this gas furnish a mixture of 2 volumes of oxygen and 1 of chlorine, its composition being thus represented:—

			By weight.		By vol.	Sp. gr.
Chlorine	...	Cl	=	35.5 or 52.59	1 or 0.5	= 1.226
Oxygen	...	O <sub>2</sub>	=	32.0 47.41	2 1.0	= 1.105
Chloric dioxide		ClO <sub>2</sub>	=	67.5 100.00	2 1.0	= 2.331

Chloric dioxide may be thus obtained:—Fused potassic chlorate is broken into coarse fragments, and treated with two-thirds of its weight of oil of vitriol, the action being favoured by a very gentle heat. The reaction may be represented by the following equation:



This peroxide may also be procured mixed with carbonic anhydride, by mixing potassic chlorate and crystallized oxalic acid, both finely powdered separately, and gently heating to  $149^{\circ}$  ( $65^{\circ}$  C.) (Calvert).

Chloric dioxide acts rapidly upon mercury, and must therefore be collected by displacement. Mere contact with many combustible matters at once determines its explosion. Place, for instance, about 0.3 grm. of potassic chlorate at the bottom of a tall glass, and pour upon it a little water; then having placed the glass in a deep plate (fig. 307), add a piece of phosphorus of about the size of a pea, and by means of a long funnel pour slowly in about a teaspoonful of oil of vitriol; flashes of a beautiful green light, attended with a crackling noise, will be immediately produced. If loaf sugar and potassic chlorate be separately powdered, and mixed in equal proportions with each other on a sheet of paper, by means of a spatula, the addition of a drop of sulphuric acid will liberate the dioxide, which will be decomposed by the combustible matter, and sufficient heat will be emitted to cause the mass to burst into flame, and to deflagrate with great brilliancy. Peroxide of chlorine is not possessed of acid properties; alkaline solutions, however, absorb it rapidly, but when evaporated, they yield a mixture of chlorite and chlorate of the metal:—

FIG. 307.





Other oxides of chlorine have been obtained; they have a composition which may be explained by considering them as compounds of chlorous anhydride with chloric or with perchloric anhydride; they, however, present but few points of interest. Davy's *euchlorine*, which is evolved on gently heating a chlorate with hydrochloric acid, is a yellow explosive gas, consisting of a mixture of chlorine with one of these compound oxides, the *chloro-chloric acid* ( $2\text{Cl}_2\text{O}_5, \text{Cl}_2\text{O}_3$ ; Millon).

(386) CHLORIDE OF NITROGEN ( $\text{HCl}_2\text{N}, \text{Cl}_3\text{N}$  ?); *Sp. Gr. of Liquid*, 1.653.—The attraction existing between chlorine and nitrogen is very feeble; the compound commonly known by the name of chloride of nitrogen is always obtained by indirect means.

If a current of ammoniacal gas be directed into a bottle of gaseous chlorine it will take fire spontaneously, burning with a green flame, whilst hydrochloric acid is formed, and nitrogen is set free; dense white fumes being generated by the union of the hydrochloric acid with undecomposed ammonia. By modifying the experiment, the reaction may be employed as a means of obtaining nitrogen gas, for when a stream of chlorine gas is transmitted through a solution of ammonia, the hydrochloric acid as fast as it is formed combines with undecomposed ammonia, and nitrogen is liberated: if the solution be concentrated, each bubble of chlorine produces a flash of light. One atom of ammonia, when decomposed by 3 atoms of chlorine, yields 1 atom of nitrogen;  $2\text{H}_3\text{N} + 3\text{Cl}_2$ , becoming  $6\text{HCl} + \text{N}_2$ . The nitrogen is apt to be mixed with a variable quantity of oxygen, a little water being also decomposed at the same time. (A. Anderson.)

But if instead of acting on a solution of free ammonia, a bottle of chlorine perfectly clear from greasy matter be inverted over a leaden dish containing a solution of 1 part of sal ammoniac ( $\text{H}_4\text{NCl}$ ), in 12 parts of water, drops of a yellow oily-looking liquid gradually collect on the surface of the liquid and fall to the bottom, whilst the chlorine slowly disappears; this liquid is the substance known as *chloride of nitrogen*. A safer method of obtaining this body consists in suspending a fragment of sal ammoniac (say 1.5 or 2 grammes) in a solution of hypochlorous acid; oily drops of the so-called chloride of nitrogen are gradually formed, and sink in the liquid as the salt is dissolved. The new body remains liquid at  $-16^\circ$  ( $-27^\circ \text{C.}$ ), but is very volatile, and possesses a peculiar penetrating odour. It is one of the most

dangerous compounds known, for it explodes with tremendous violence when heated to between  $200^{\circ}$  and  $212^{\circ}$  ( $93^{\circ}$  and  $100^{\circ}$  C.), emitting a flash of light when the detonation occurs. The explosion is so sudden that it invariably breaks any glass or porcelain vessel in which it may be contained: hence a leaden saucer is used in preparing the compound. The liquid chloride also explodes violently at ordinary temperatures when brought into contact with many inflammable substances, such as oil of turpentine, phosphorus, and the fixed oils. The alkalis likewise cause its immediate explosion. On the other hand, it does not explode when touched with the resins, the strong acids, with metallic bodies in general, or with sugar.

Little or nothing is known of the cause of these remarkable reactions, or of the light and heat emitted when the chloride explodes by slightly elevating its temperature; in this case and in the analogous instances of the explosion of the oxides of chlorine, light is emitted, not during the act of combination, as is usual, but during the expansion and sudden separation of the two gaseous elements.

The analysis of this body is attended with great difficulty. It is a substitution product obtained from ammonia, the hydrogen of which has been more or less completely displaced by chlorine; and it is highly probable that it is not simply a chloride of nitrogen, but a combination of chlorine, nitrogen, and hydrogen ( $\text{HCl}_2\text{N}, \text{Cl}_3\text{N}$ ), somewhat analogous to the corresponding explosive compound which may be formed with iodine (400).

(387) CHLORIDES OF CARBON.—Chlorine does not unite directly with carbon, but Faraday succeeded in procuring several compounds between these elements by the decomposition of Dutch liquid, a combination of carbon and hydrogen with chlorine, obtained under circumstances which will be explained when treating of olefiant gas (488).

*Acetylene chloride* (formerly *Subchloride*) of carbon ( $\text{C}_2\text{Cl}_4 = 95$ ) forms fine silky crystals, which may be sublimed in closed vessels without change; it is soluble in ether. This substance is obtained by decomposing the ethylene-chloride of carbon ( $\text{C}_2\text{Cl}_4$ ), by causing it to pass several times through a tube heated to bright redness. If heated in air on platinum foil, it burns with a red smoky flame.

*Ethylene chloride* (formerly *Protochloride*) of carbon ( $\text{C}_2\text{Cl}_4 = 166$ ); *Sp. Gr. of Liquid*, 1.619; *of Vapour*, 5.82; *Mol. Vol.* [ ] ; *Rel. wt.* 83; *Boiling pt.*  $24.8^{\circ}$  ( $120^{\circ}$  C.).—This compound was procured by Faraday from the solid chloride ( $\text{C}_2\text{Cl}_4$ ) by subliming it repeatedly through a tube filled with fragments of glass heated to redness. It is a transparent colourless liquid, with an aromatic odour.

*Faraday's chloride* (formerly *Sesquichloride*) of carbon ( $\text{C}_2\text{Cl}_6$ ,

=237); *Sp. Gr. of Solid*, 2.0; *of Vapour*, 8.157; *Mol. Vol.* [ ]; *Rel. wt.* 118.5; *Melting-pt.* 320° (160° C.); *Boiling-pt.* 360° (182° C.). —This chloride was originally procured by the action of chlorine upon Dutch liquid (488); but it has since been obtained by the action of chlorine upon a variety of derivatives from the alcohol series. It is a volatile crystalline solid, with an aromatic odour resembling that of camphor. It is soluble in alcohol, in ether, and in the fixed and volatile oils. An isomeric (506) liquid trichloride, the vapour of which has a density of 4.082, and a composition  $\text{CCl}_3$ , was obtained by Regnault by passing the vapour of tetrachloride of carbon ( $\text{CCl}_4$ ) through a tube heated to low redness.

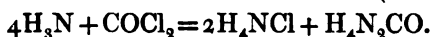
*Tetrachloride* (formerly *Bichloride*) *of Carbon* ( $\text{CCl}_4=154$ ); *Sp. Gr. of Liquid*, 1.599; *of Vapour*, 5.30; *Mol. Vol.* [ ]; *Rel. wt.* 77; *Freezing-pt.*  $-9^\circ$  ( $-23^\circ \text{C.}$ ); *Boiling-pt.*  $172^\circ$  ( $78^\circ \text{C.}$ ). —This substance was obtained by Regnault from wood-spirit, from chloroform, and from other derivatives from wood-spirit, by exposing them in the sun to the action of an excess of chlorine. Kolbe also found that a mixture of the vapour of carbonic disulphide and dried chlorine, when passed through a porcelain tube heated to redness, yields the same compound mixed with chloride of sulphur;  $\text{CS}_2 + 3\text{Cl}_2 = \text{CCl}_4 + \text{S}_2\text{Cl}_2$ . If the mixture be agitated with a solution of potash, the chloride of sulphur is decomposed and dissolved, and the tetrachloride subsides; it may be decanted and purified by distillation. It is a colourless liquid, which is insoluble in water, but soluble in alcohol and in ether; an alcoholic solution of potash decomposes it into chloride and carbonate of potassium;  $6\text{KHO} + \text{CCl}_4 = 4\text{KCl} + \text{K}_2\text{CO}_3 + 3\text{H}_2\text{O}$ . If its vapour diluted with air be respired, it exerts an anæsthetic action on the system. Tetrachloride of carbon becomes a crystalline solid of pearly lustre at  $-9^\circ$ . If passed through red-hot tubes it is decomposed into free chlorine and a mixture of ethylene-chloride and Faraday's sesquichloride of carbon.

(388) **CARBONIC OXYDICHLORIDE**; *Chlorocarbonic Acid*; *Phosgene Gas* ( $\text{COCl}_2=99$ ); *Rel. wt.* 49.5; *Theoretic Sp. Gr.* 3.42; *Observed*, 3.68; *Mol. Vol.* [ ]. —When equal measures of carbonic oxide and chlorine are exposed to the direct rays of the sun, they combine, and become condensed into half their volume. The combination takes place slowly in the diffused light of day; but no action occurs if the two gases are mixed together and kept in a dark room. There are other modes of obtaining this compound indirectly; for example, it may be prepared by transmitting carbonic oxide gas through heated antimonious chloride ( $\text{SbCl}_3$ );

the action of light is not necessary in this case. This reaction may sometimes be usefully employed as a test for carbonic oxide when mixed in small quantity with other gases, the pungent odour of the oxydichloride which is formed being very characteristic. The composition of the gas is the following :—

		By weight.		By vol.		Sp. gr.
Carbonic oxide	CO	=	28 or 28·28	2 or 1·0	=	0·967
Chlorine	Cl <sub>2</sub>	=	71 71·72	2 1·0	=	2·453
Phosgene gas	COCl <sub>2</sub>	=	99 100·00	2 1·0	=	3·420

Carbonic oxydichloride is a colourless, suffocating gas, which is immediately decomposed by water into carbonic anhydride and hydrochloric acid :  $\text{COCl}_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{HCl}$ . A similar decomposition occurs if it be treated with many of the metallic oxides, such as zincic oxide, whilst a chloride of the metal is formed ;  $\text{COCl}_2 + \text{ZnO} = \text{CO}_2 + \text{ZnCl}_2$ . If heated with arsenicum or antimony, the chlorine is removed and carbonic oxide is liberated. Carbonic oxydichloride does not possess the characters of an acid ; but if the gas be mixed with ammonia in the proportion of 1 volume of phosgene to 4 volumes of ammonia, both gases are condensed, and form a white volatile solid, which is neutral to test-paper, destitute of smell, and soluble in water and in alcohol slightly diluted, but insoluble in ether. This substance consists of a mixture of ammonic chloride and carbamide (urea ; Natanson) :



## § II. BROMINE : Br.=80.\*

*Atomic Vol. of Vapour*  $\square$  ; *Rel. wt.* 80 ; *Theoretic Sp. Gr. of Vapour*, 5·528 ; *Observed*, 5·54 ; *of Liquid at 32° (0° C.)* 3·187 ; *Melting-pt.* 9°·5 (−12°·5 C.) ; *Boiling-pt.* 145°·4 (63° C.) ; *Monad, as in HBr.*

(389) BROMINE, so named owing to its irritating odour (from *βρώμος*, a stench), was discovered by Balard in the year 1826, in *bittern*, which is the mother-liquor of sea-water after the less soluble salts have been extracted by crystallization. Bromine exists in sea water in minute quantity, varying from one-third of a grain to about one grain in each gallon, or from 4 to 14 mgrms. per litre ; the waters of the Dead Sea also contain bromine in even larger quantity than this : it appears to be combined with magnesium, as bromide of magnesium. Many saline springs, such as those of Kreuznach and Kissingen, likewise contain bromine

\* The molecular volume of *free* bromine is regarded as  $(\text{BrBr}) = \square$  ; and its *molecular weight* = 160.



in quantity sufficient to render its extraction from them a source of profit. Indeed, few deposits of sodic chloride exist in which traces of bromine have not been discovered. It has also been found in a silver ore from Mexico, and it is abundant in the mines of Chañarcillo, in South America; in both cases the bromide of silver is mixed with chloride of silver.

*Extraction.*—In order to obtain bromine, the mother-liquor from the brine, after all the salts separable by crystallization have been removed, is subjected to a current of chlorine, taking care to avoid an excess of this gas, which would occasion inconvenience by forming a compound with the liberated bromine. All the bromides are decomposed readily by chlorine, the attraction of chlorine for the metals being more powerful than that of bromine. In the foregoing operation magnesian chloride is formed, and bromine is set free:  $\text{MgBr}_2 + \text{Cl}_2 = \text{MgCl}_2 + \text{Br}_2$ ; the bromine shows itself by giving to the liquid a beautiful and characteristic yellow colour. This yellow liquid when agitated with ether, parts with its bromine, which is dissolved by the ether. If the mixture be allowed to stand in a glass globe closed at the top by a stopper, and furnished with a glass stopcock at the bottom, the ether rises to the surface, where it forms a beautiful golden yellow layer. The mother-liquor is drawn off by opening the stopcock, and the ethereal solution is agitated with a solution of potassic hydrate; the yellow colour immediately disappears; bromide and bromate of potassium are formed and dissolved in the water;  $3\text{Br}_2 + 6\text{KHO} = \text{KBrO}_3 + 5\text{KBr} + 3\text{H}_2\text{O}$ ; whilst the ether, after repose, rises again to the surface despoiled of its bromine, and may again be employed in a repetition of the process upon a fresh quantity of bittern. When the solution of potash has, by repeated charges of bromine, been nearly neutralized, the liquid is evaporated to dryness; the saline mass is gently ignited to decompose the bromate, after which it is mixed with peroxide of manganese and distilled in a retort with sulphuric acid: dense red vapours of bromine pass over, which may be collected in a receiver containing water, and kept cool by ice. The decomposition is of the same nature as that attending the liberation of chlorine from sea salt by means of oxide of manganese and sulphuric acid:—



In this operation a small quantity of chlorine passes over with the bromine; since from the manner in which potassic bromide is formed, it is always contaminated with a portion of potassic

chloride. The chlorine unites with part of the bromine, forming chloride of bromine, which is partially decomposed and dissolved by the water in the receiver, while the bromine is condensed in red drops. In order to obtain bromine free from chlorine it must be saturated with baric hydrate, which produces a mixture of bromide and chloride with bromate of barium: this mixture must be heated to redness in order to convert the bromate into bromide of barium, and the residue digested in alcohol, which dissolves nothing but the bromide. The baric bromide is obtained by evaporation of its alcoholic solution, and when heated with black oxide of manganese and sulphuric acid it yields pure bromine.

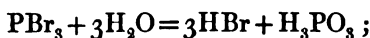
*Properties.*—Bromine forms a red liquid, so deep in colour as to be nearly opaque. It has a sp. gr. of 2.966 at 59° (15° C.): it is very volatile, and emits dense red vapours resembling peroxide of nitrogen in colour (Part I. fig. 81). In smell it resembles chlorine, and is extremely irritating to the nose and fauces when respired, even if largely diluted with air. When swallowed it operates as a powerfully irritating poison; it acts rapidly on all the organic tissues, and renders the skin permanently yellow. Bromine boils at 145°.4 F. (63° C.) (Pierre), and when exposed to a temperature of 9°.5 (−12°.5 C.) it forms a red crystalline solid. The properties of bromine greatly resemble those of chlorine, though they are less strongly developed. It bleaches many vegetable colours. Its vapour will not support the flame of a burning taper. Bromine is slightly soluble in water, and gives to it a yellow colour; it also forms with it a hydrate ( $\text{Br} \cdot 5\text{H}_2\text{O}$ ; Löwig), which crystallizes in octohedra at 32° (0° C.). The aqueous solution of bromine is decomposed by sunlight into hydrobromic acid and oxygen. Alcohol dissolves bromine freely, and ether does so still more abundantly. Olefiant gas is rapidly absorbed by liquid bromine, and a liquid compound ( $\text{C}_2\text{H}_4\text{Br}_2$ ), ethylene dibromide, is formed. Bromine combines directly with phosphorus, and with many of the metals, forming compounds termed *bromides* (540), the act of combination being often attended with ignition, as in the case of antimony and of tin: even gold combines with it, though but slowly; its compound with silver furnishes a material of considerable value in photographic operations.

(390) HYDROBROMIC ACID; *Hydric bromide* ( $\text{HBr}=81$ ); *Rel. wt.* 40.5; *Theoretic Sp. Gr.* 2.7986; *Observed*, 2.731; *Mol. Vol.*  .—Bromine resembles chlorine in its property of combining with hydrogen, and forming with it a very powerful acid, which is a gaseous body consisting of equal measures of hydrogen and bromine vapour united without change of bulk. The mixture

of bromine vapour and hydrogen cannot be detonated by the approach of flame, or by the electric spark, but the two elements may be made to unite slowly, by suspending a red-hot platinum wire in the mixture. If moisture be present, the occurrence of combination instantly shows itself by the formation of white fumes, which arise from the union of the newly produced gaseous acid with the aqueous vapour.

*Preparation.*—1. Hydrobromic acid gas may be procured abundantly by decomposing potassic bromide with a concentrated solution of phosphoric acid. If sulphuric acid be used for the purpose, the product is impure, since this acid itself undergoes partial deoxidation.

2.—It may also be obtained by decomposing phosphorous bromide by means of a small quantity of water, when the following reaction occurs:—



phosphorous and hydrobromic acids being produced. This experiment may be easily performed with the aid of a tube bent as in

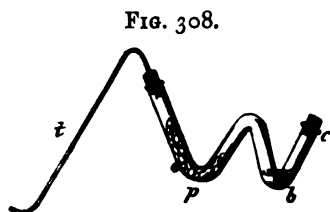


FIG. 308.

fig. 308. In the bend *p*, a few fragments of phosphorus and moistened glass are placed, bromine is poured into *b*, and the tube is closed by a cork, *c*; on applying a gentle heat at *b*, the bromine is distilled over and comes into contact with the phosphorus, forming the tri-

bromide, which is decomposed by the water at the moment of its formation, and hydrobromic acid escapes by the bent tube, *t*.

Hydrobromic acid gas is colourless, it is not inflammable, it extinguishes flame, and possesses the usual irritating action of acid gases on the lungs. Faraday succeeded in liquefying the gas under strong pressure, and in a bath of solid carbonic anhydride and ether, he even obtained it in the form of a solid, which melted at  $-124^\circ$  ( $-87^\circ$  C.). The acid has the following composition:—

		By weight.	By volume.	Sp. gr.
Bromine ...	Br = 80	or 98.76	1 or 0.5	= 2.764
Hydrogen ...	H = 1	1.24	1	0.5 = 0.034
Hydrobromic acid ... }	HBr = 81	100.00	2	1.0 = 2.798

Hydrobromic acid gas is very soluble in water, forming, when concentrated, a fuming solution of greater density than hydrochloric acid. A solution of the acid of sp. gr. 1.486 ( $\text{HBr}, 5\text{H}_2\text{O}$ ) contains about 47 per cent. of the anhydrous acid; it boils at

259° (126° C.), and may be distilled without change. (See *note*, p. 152.) Chlorine decomposes it immediately; bromine being set free and hydrochloric acid produced.

The action of hydrobromic acid upon the metallic oxides is analogous to that of hydrochloric acid upon them; bromide of the metal and water being produced; for instance, hydrobromic acid and potassic hydrate form potassic bromide and water;  $\text{KHO} + \text{HBr}$  yielding  $\text{KBr} + \text{H}_2\text{O}$ .

(391) *Bromides*.—The bromides are all solid at ordinary temperatures: most of them are fused by a moderate heat, and are partially volatilized; and the bromides of gold and platinum are decomposed. Most of the bromides are readily soluble in water. They are all decomposed by chlorine, and when in solution they may be recognized by the yellow colour of bromine which is produced by the addition of a few drops of chlorine water, taking care to avoid an excess of chlorine. On agitating this yellow solution with ether, the bromine is dissolved by the ether, which on standing separates as a yellow liquid, at the top of the colourless aqueous portion. If the quantity of the bromide is very minute, a small quantity of carbonic disulphide may be advantageously substituted for ether, as it acquires a yellow tinge with an amount of bromine too small to act upon the ether; the presence of sulphuric or of sulphurous acid must however in this case be avoided. The bromides, when heated with black oxide of manganese and oil of vitriol, yield red vapours of bromine; strong nitric acid has a similar effect. Both argentic and plumbic nitrate give a white precipitate with solutions of the bromides, forming argentic bromide ( $\text{AgBr}$ ), or plumbic bromide ( $\text{PbBr}_2$ ); argentic bromide is insoluble in cold nitric acid, but is dissolved by a large excess of ammonia; but plumbic bromide is dissolved by the addition of diluted nitric acid. Mercurous nitrate also gives a white precipitate of mercurous bromide ( $\text{HgBr}$ ) when added to solutions of the bromides; it is soluble in chlorine water with liberation of bromine. Cupreous bromide is also sparingly soluble.

Bromine often combines with the same metal in more than one proportion, and the compounds of bromine correspond almost always, both in number and composition, with those of chlorine with the same metal. Oxybromides may be formed resembling the oxychlorides; and the bromides of the alkali-metals form double bromides with the bromides of the metals which yield acids with oxygen.

(392) BROMIC ACID; *Hydric bromate* ( $\text{HBrO}_3 = 129$ ).—The oxyacids of bromine are, with the exception of bromic acid, nearly unknown, and this com-

pound has never been obtained in the form of anhydride. The bromic corresponds to chloric acid in composition. Potassic bromate is procured by acting on bromine with caustic potash, and from this salt the acid is obtained by a process similar to that employed in the preparation of chloric acid (382). By the action of heat, potassic bromate is decomposed, potassic bromide being formed, whilst oxygen is liberated. Any solid bromate, when mixed with concentrated sulphuric acid and heated, gives off red fumes of free bromine, while oxygen is evolved. Argentic and mercurous bromate are anhydrous and sparingly soluble: plumbic bromate retains 1 atom of water ( $\text{Pb}_2\text{BrO}_5 \cdot \text{H}_2\text{O}$ ); it likewise is but slightly soluble. When heated with hydrochloric acid these precipitates evolve free bromine. All the salts of bromic acid which have as yet been prepared are monobasic. A *hypobromous acid* ( $\text{HBrO}$ ), which is very unstable, may, it is said, be formed by agitating finely powdered mercuric oxide with bromine and water. Compounds of feeble bleaching powers may also be obtained by treating bromine with solutions of the alkalies.

*Perbromic acid*; *Hydric perbromate* ( $\text{HBrO}_4 = 145$ ) was obtained by Kammerer by decomposing perchloric acid by the gradual addition of bromine to its solution.

(393) *Bromous chloride* ( $\text{BrCl}$ , ?), is easily obtained by transmitting chlorine gas through liquid bromine: it is a volatile, reddish-yellow liquid, with a very pungent, irritating odour. Water dissolves it, forming a deep yellow solution possessed of considerable bleaching power.

*Bromide of Nitrogen* may be obtained by digesting potassic bromide with the so-called chloride of nitrogen; it forms a detonating oily-looking liquid, resembling chloride of nitrogen in appearance and properties.

According to Schiel, a *carbonic oxydibromide* ( $\text{COBr}_2$ ) analogous to phosgene may be obtained by the action of bromine vapour on carbonic oxide in the sun's rays.

### § III. IODINE: $\text{I} = 127$ .\*

*Atomic and Comb. Vol. of Vapour*  $\square$ ; *Rel. wt.* 127; *Theoretic Sp. Gr. of Vapour*, 8.756; *Observed*, 8.716; *Sp. Gr. of Solid*, 4.947; *Melting-pt.*  $225^\circ$  ( $107^\circ \text{C.}$ ); *Boiling-pt.*  $347^\circ$  ( $175^\circ \text{C.}$ ); *Monad as in HI, rarely Triad as in  $\text{ICl}_3$ .*

(394) IODINE, the third element in the group which we are now examining, is still denser than bromine, as it assumes the solid form at the ordinary temperature of the air. It was discovered in the year 1811, when it was found by Courtois accidentally, in the waste liquors produced in the manufacture of sodic carbonate from the ashes of sea-weed.

Iodine exists in the ocean in quantities still smaller than bromine. It is, notwithstanding, obtained with less difficulty, since the fuci, algæ, sponges, and other marine plants, extract it

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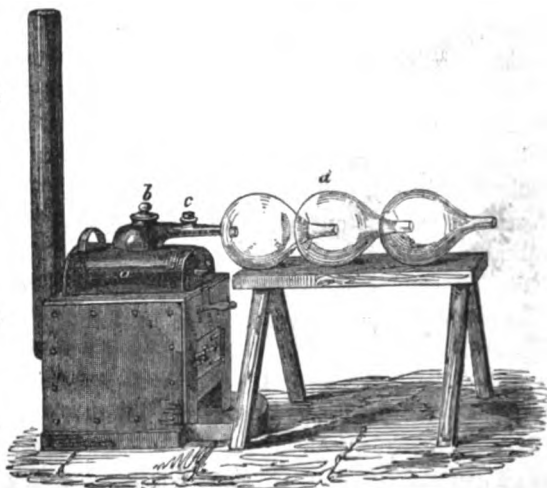
\* Taking the molecule of iodine when free to be  $(\text{I I})$  or  $\text{I}_2$ , its molecular volume in the state of vapour will be  $\square$ , and its molecular weight = 254.

from sea-water, and store it up in their tissues. These, when burnt, give an ash which is technically known as *kelp*; it contains iodine in the form of sodic iodide. In the mineral kingdom, iodine has been found in one or two rare ores; thus it occurs combined with silver in Mexico, and with zinc in Silesia; it also exists in small quantity as iodate in the crude Peruvian sodic nitrate.

**Extraction.**—Iodine is at present largely manufactured at Glasgow, from kelp made on the coasts of Scotland and Ireland; the following is an outline of the process adopted in procuring it:—The sea-weed, having been dried in the sun, is burned in shallow excavations, at a low heat; owing to the volatility of the sodic iodide at a red heat, the loss of this salt would be considerable if the temperature were allowed to rise too high. The half-fused ash, or kelp, which remains, is broken into fragments and treated with boiling water, which dissolves about one-half of the ash. The liquid thus obtained is then evaporated in open pans, and all that can be separated by crystallization is removed; a double sulphate of potassium and sodium, sodic carbonate, and potassic chloride are thus extracted. The iodine remains in the mother-liquor, which still retains disodic sulphide, besides sodic hyposulphite, and some carbonate. This liquor, or *iodine ley*, of specific gravity from 1.33 to 1.38, is now mixed with one-eighth of its bulk of oil of vitriol, and allowed to stand for twenty-four hours; carbonic anhydride, sulphurous anhydride, and sulphuretted hydrogen gases escape, and sodic

sulphate crystallizes out, mixed with a considerable quantity of deposited sulphur. The supernatant liquid is next transferred to a stoneware or leaden retort, which, if of lead, is of cylindrical form, *a*, fig. 309, supported in a sand-bath, and gently heated from beneath by a small fire; the head of the retort, *b, c*, is luted on

FIG. 309.



with clay, and the contents of the retort, having been heated to about  $140^{\circ}$  ( $60^{\circ}$  C.), a quantity of powdered black oxide of manganese is introduced through the tubulure, *b*. The process must be conducted slowly, at a low temperature; iodine distils over, and is condensed in the globular receivers, *d*. It is purified by a second sublimation. The object of the second tubulure, shown at *c*, is to facilitate the clearing of the neck of the retort in case it should become obstructed by the formation of crystals. If the temperature be allowed to rise as high as  $212^{\circ}$ , the sodic chloride retained in the ley is decomposed, chlorine is disengaged, and combines with part of the iodine, forming chloride of iodine, which is wasted.

In the foregoing process, the addition of the sulphuric acid occasions the decomposition of the sodic carbonate and hyposulphite, which still remain in solution, as well as of any disodic sulphide that may be present, forming sodic sulphate which is removed by crystallization. The liquid retains an excess of sulphuric acid, and all the sodic iodide. When this mixture is heated with peroxide of manganese, the iodine is liberated, whilst hydro-sodic sulphate and manganous sulphate remain in the retort. The process resembles that for chlorine and for bromine:—



*Properties.*—The crystalline form of iodine is an octohedron with a rhombic base; but it is generally obtained in bluish-black scales, resembling plumbago in lustre. It is a non-conductor of electricity. At ordinary temperatures, and especially when in a moist condition, it is sensibly volatile, emitting an odour like that of chlorine, but much weaker; when heated it undergoes fusion at  $225^{\circ}$ ; and at about  $347^{\circ}$  it boils and is converted into a magnificent purple vapour, whence it derives its name (from *ἰοειδής*, violet-coloured). Iodine, when taken internally, acts in large doses as an irritant poison; but in small quantities it is a very valuable medicine, particularly in glandular swellings, and in certain forms of goître. It stains the skin and most organized substances of a brown colour, and gradually corrodes them. Water forms with it a yellow solution, but dissolves it only in very small quantity. Its bleaching properties are very feeble. Alcohol, ether, hydriodic acid, and solutions of the iodides, dissolve it freely, forming brown solutions. *Lugol's Solution*, which was formerly much used in medicine, consists of 2 parts of iodine and 3 of potassic iodide, dissolved in 44 parts of water; it is of a

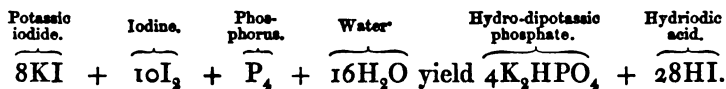
deep brown colour. Iodine is also soluble in carbonic disulphide, to which a minute quantity of iodine imparts a characteristic rich violet colour. A strong solution of iodine in the disulphide is opaque to light, but it allows the less refrangible heat rays to pass freely. Chloroform, carbonic tetrachloride, and benzol likewise dissolve iodine, forming red solutions. Iodine attacks many of the metals rapidly, forming compounds termed *iodides*; iron or zinc is readily dissolved by it if placed with it in water, an iodide of the metal being formed. The compounds of iodine with the metals and with hydrogen are decomposed by chlorine, and even by bromine, while the iodine is set free. Advantage is taken of this fact in ascertaining the presence of iodine. The most delicate test for it, when uncombined, is the intense blue colour which it yields with starch; by its means, with due precaution, 1 part of iodine, when dissolved in one million parts of water, may be discovered.

There are various modes of applying this test: the simplest consists in mixing a little cold starch paste with the liquid which is suspected to contain iodine; if it be present in an uncombined form, a beautiful blue colour shows itself. If the iodine be in combination, this colour does not appear until a drop of chlorine water or of solution of bleaching powder be added to set the iodine free. An excess of chlorine must be avoided, as it forms chloride of iodine, and prevents the action of the test: David Price recommends the use of a solution of potassic nitrite as a substitute for the chlorine, the liquid to be tested being slightly acidulated: no inconvenience arises from the presence of the nitrite in slight excess. The colour fades away if the solution be heated, but it is partially restored as the temperature falls. Solutions of the alkalies, as well as of sulphurous acid, sulphuretted hydrogen, and reducing agents generally, destroy the colour. As starch paste cannot be long kept without undergoing decomposition, it is often convenient to substitute for the freshly made paste, paper which has been smeared with the starch, and allowed to become dry. If kept in a dry place, such paper may be preserved for an indefinite length of time, and is ready for use at any moment.

(395) HYDRIODIC ACID; *Hydric iodide*,  $\text{HI}=128$ ; *Rel. wt.* 64; *Theoretic Sp. Gr.* 4.4125; *Observed*, 4.443; *Mol. Vol.*  .—By heating iodine in hydrogen, the volume of the gas becomes doubled, and a colourless acid gas is produced; but it is never prepared for use in this manner. A better mode is the following:—Place in a small retort 10 parts of potassic iodide



with 5 of water, and 20 of iodine; then drop in cautiously 1 part of phosphorus cut into small fragments, and apply a gentle heat. Hydriodic acid gas will be extricated abundantly, and may be collected, by displacement, in dry bottles. The iodide of phosphorus is first formed, and this is decomposed by water into hydriodic and phosphoric acids, whilst a fresh portion of hydriodic acid is liberated by the action of the phosphoric acid on the potassic iodide. The final result of the reaction is exhibited by the following equation:—



Hydriodic acid gas is not combustible, nor does it support combustion. It fumes in the air, and possesses a powerfully acid irritating odour. It is reduced under strong pressure to a yellowish liquid, which freezes at  $-60^\circ$  ( $-51^\circ$  C). Water dissolves the gas with great avidity.

A solution of hydriodic acid may be easily prepared by suspending iodine in water, and transmitting a current of sulphuretted hydrogen gas through the mixture until the brown colour of the iodine disappears; sulphur is deposited in abundance, and hydriodic acid is formed. The liquid gradually becomes clear if left at rest; it may then be decanted from the precipitated sulphur: the decomposition consists simply in the displacement of the sulphur by the iodine;  $2\text{H}_2\text{S} + 2\text{I}_2$  becoming  $4\text{HI} + \text{S}_2$ . This liquid may be concentrated till it acquires a density of 1.7, when it consists of  $(2\text{HI}, 11\text{H}_2\text{O}; \text{Bineau})$ .\* It then distils unchanged at  $262^\circ$  ( $128^\circ$  C.). It is a powerful acid, and dissolves iodine freely, forming a brown solution: by exposure to the air, especially if placed in a strong light, it absorbs oxygen, water is formed, and the liquid becomes brown from the liberation of iodine. Chlorine effects its instant decomposition, whether it be in the gaseous form or in solution. Bromine and nitric acid act similarly and with almost equal rapidity; many other oxidizing agents also decompose it. Mercury decomposes it gradually, and combines with its iodine. A solution of hydriodic acid dissolves

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\* Roscoe has shown that, both in this case and in the analogous one of the solution of hydrobromic acid, the constancy of the boiling-point, as well as the apparent definite character of the hydrate, is accidental, and dependent upon causes similar to those traced in hydrochloric acid. (*Note*, p. 123.) Hydrofluoric acid evidently furnishes a true hydrate, but it was found to be partially decomposed by varying the temperature of evaporation.

many of the metals, such as zinc and iron, with evolution of hydrogen and formation of a metallic iodide.

The composition of hydriodic acid may be ascertained by heating potassium in a measured volume of the gas. Potassic iodide is formed, and hydrogen remains equal in bulk to half the acid gas employed; consequently its composition may be thus represented:—

		By weight.		By vol.		Sp. gr.
Iodine ... ..	I	= 127	or 99'21	1	or 0'5	= 4'378
Hydrogen ... ..	H	= 1	0'79	1	0'5	= 0'034
Hydriodic acid HI		128	100'00	2	1'0	4'412

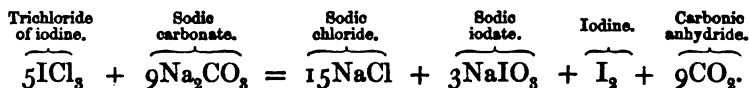
(396) *Iodides*.—The iodides of the metals are all solid at ordinary temperatures; they are less fusible and volatile than the corresponding chlorides and bromides. The iodides of gold, silver, platinum, and palladium are decomposed by heat alone, whilst the metals are left in a state of purity; but most of the iodides are converted into oxides when heated in the air,—the oxygen displacing the iodine. All the iodides, whether solid or in solution, are decomposed by chlorine and bromine, as well as by nitrous acid and concentrated nitric acid, with liberation of iodine. Iodine is also set free when an iodide is heated with oil of vitriol and peroxide of manganese, and violet vapours of iodine are obtained. Water dissolves the greater number of the metallic iodides freely; some of them are insoluble, and exhibit colours of great brilliancy. The iodides of some of the metals which form acids with oxygen, such as those of tin, arsenic, and antimony, are decomposed by water. The soluble iodides of the metals may be obtained by the direct action of hydriodic acid upon the metallic oxide, or by the action of iodine and water upon the metal itself. These iodides, when in solution, are characterized by the reaction with starch already mentioned (394). With a solution of corrosive sublimate ( $\text{HgCl}_2$ ) they give a beautiful salmon-coloured precipitate, which almost immediately changes to a brilliant scarlet: this is mercuric iodide: it is soluble in excess both of potassic iodide and of corrosive sublimate. Mercurous nitrate gives a green precipitate in solutions of the soluble iodides. With plumbic nitrate they yield a bright yellow precipitate of plumbic iodide, which is slightly soluble in boiling water, especially if the lead salt be present in excess; on cooling, the plumbic iodide is deposited in very beautiful silky scales. With argentic nitrate a buff-coloured argentic iodide, nearly insoluble in ammonia, is formed, but it is freely soluble in sodic hyposulphite and in potassic cyanide. If a mixture of ferrous

sulphate and cupric sulphate be added to a solution of any iodide, a white cupreous iodide ( $\text{CuI}$ ) is precipitated. With auric chloride the iodides give a lemon-yellow precipitate; and with salts of palladium a brown palladious iodide ( $\text{PdI}_2$ ) is produced, which is sometimes used for ascertaining the quantity of iodine present in a solution in which it occurs mixed with chlorine, since palladious chloride is freely soluble in water (541).

(397) **OXIDES OF IODINE.**—Iodine has a more powerful attraction for oxygen than either chlorine or bromine, and forms with it two compounds which by their action upon water furnish well-defined acids, viz., the iodic ( $\text{HIO}_3$ ) and the periodic acid ( $\text{HIO}_4$ ) besides some other oxides but imperfectly known.

**IODIC ANHYDRIDE** ( $\text{I}_2\text{O}_5=334$ ); *Comp. in 100 parts*; I 76.04; O 23.96.—This body may be obtained by the cautious application of heat to iodic acid.

**Iodic acid; Hydric iodate** ( $\text{HIO}_3=176$ ).—This acid corresponds in composition to chloric and bromic acids. It may be prepared in several ways. 1.—It may be procured by long boiling of iodine in concentrated nitric acid. 2.—Equal parts of potassic chlorate and iodine may be mixed with 5 parts of water and a little nitric acid; chlorine is thus evolved in abundance, whilst potassic iodate is formed and dissolved in the liquid: the chloric acid which is set free in the first instance by the nitric acid imparts its oxygen to the iodine, chlorine gas escaping, while the iodic acid liberates a fresh portion of chloric acid from the chlorate, and this undergoes a similar decomposition (Millon). 3.—Liebig's plan of preparing iodic acid consists in suspending iodine in water, and transmitting through it a current of chlorine gas till the iodine is dissolved; the liquid is then neutralized by sodic carbonate, when a copious effervescence ensues, attended by a precipitate of iodine, which may be again treated similarly by chlorine. In this case the chlorine combines directly with the iodine and forms trichloride of iodine, which is dissolved by water unaltered: it is decomposed on the addition of the alkaline carbonate in the following manner:—



The neutralized liquid contains sodic iodate and chloride. Baric chloride is next added; an abundant precipitate of baric iodate, which is but sparingly soluble, is formed; this is washed from adhering salts, and is decomposed by a quantity of sulphuric acid

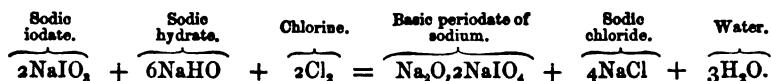
just sufficient to combine with the barium: iodic acid is dissolved by the water, whilst the insoluble baric sulphate is separated.

Iodic acid may be obtained by spontaneous evaporation of its aqueous solution in crystals composed of  $3\text{HIO}_3$ : at a temperature of  $266^\circ$  ( $130^\circ\text{C.}$ ) it loses two-thirds of its water, and becomes  $(\text{HIO}_3)_2\text{I}_2\text{O}_5$ , or by raising the heat to  $360^\circ$  ( $182^\circ\text{C.}$ ) it is converted into the anhydride, and at about  $700^\circ$  ( $371^\circ\text{C.}$ ) it is decomposed into iodine and oxygen. Its solution is destitute of odour, and has a sour, astringent taste: many organic bodies decompose it, and owing to this circumstance litmus-paper is first reddened and afterwards bleached by it.

*Iodates.*—Iodic acid offers some anomalies in its combination with bases. Some iodates contain 1 atom, some 2, and some 3 atoms of anhydride to 1 atom of base: for example, there are three iodates of sodium; they may be represented by the following formulæ:— $(\text{NaIO}_3, \text{H}_2\text{O})$ , sometimes with  $5\text{H}_2\text{O}$ ), the normal iodate;  $(2\text{NaIO}_3, \text{I}_2\text{O}_5)$ , or  $\text{Na}_2\text{I}_4\text{O}_{11}$ , the diniodate;  $(\text{NaIO}_3, \text{I}_2\text{O}_5)$ , or  $\text{NaI}_3\text{O}_8$ , the triiodate, the last two being anhydro-salts. All the iodates are decomposed by heat, and give off oxygen: if the metal have a stronger attraction for iodine than for oxygen, an iodide of the metal is formed; for instance, potassic iodate,  $2\text{KIO}_3$  becomes  $2\text{KI} + 3\text{O}_2$ : but if the attraction of the metal be greater for oxygen than for iodine, the oxide is left behind: baric iodate, for example, is converted into baryta, oxygen gas, and free iodine, the latter escaping with oxygen in violet vapours;  $2(\text{Ba}_2\text{IO}_3)$  yielding  $2\text{BaO} + 5\text{O}_2 + 2\text{I}_2$ . The iodates of the metals of the alkaline earths, if not heated too strongly, leave a basic periodate, the barium salt consisting of  $(\text{Ba}_2\text{IO}_4, 4\text{BaO})$ . The aqueous solutions of the iodates are decomposed by sulphurous acid; for example,  $\text{KIO}_3 + 3\text{H}_2\text{SO}_3 = \text{KI} + 3\text{H}_2\text{SO}_4$ ; an iodide of the metal is formed, and then the iodine may be discovered by the starch test in the usual way. With the exception of the iodates of the alkali-metals the iodates are but sparingly soluble. The calcium salt retains  $6\text{H}_2\text{O}$ ; those of strontium, and barium  $(\text{Ba}_2\text{IO}_3, \text{H}_2\text{O})$  if precipitated from hot solutions, retain  $\text{H}_2\text{O}$ ; whilst the iodates of lead and silver are anhydrous: argentic iodate is insoluble in diluted nitric acid. Iodic acid forms crystallizable compounds with the sulphuric and many other acids.

(398) PERIODIC ACID; *Hydric periodate*;  $(\text{HIO}_4 = 192)$ .—This acid corresponds in composition to the perchloric: the anhydride is at present unknown. The acid is obtained by transmitting a current of chlorine gas through a solution of sodic iodate, to which caustic soda has been added in the proportion of 3 atoms of free alkali to 1 atom of sodic iodate: an unusual decomposition takes

place, giving rise to a sparingly soluble basic sodic periodate. The reaction which occurs may be represented by the following symbols :—



The hydrated basic sodic periodate, which when crystallized contains  $(\text{Na}_2\text{O}, 2\text{NaIO}_4, 3\text{H}_2\text{O})$  is dissolved in diluted nitric acid, and precipitated by the addition of argentic nitrate; the argentic periodate is then dissolved in boiling nitric acid; a normal argentic periodate  $(\text{AgIO}_4)$  crystallizes as the liquid cools, and this salt when treated with water is decomposed into a basic argentic periodate, which is insoluble, and periodic acid, which is dissolved. By evaporation of the solution, the periodic acid may be obtained in deliquescent oblique rhombic prisms  $(\text{HIO}_4, 2\text{H}_2\text{O})$ , which are somewhat soluble in alcohol and in ether. The periodates are most of them sparingly soluble in water, but are dissolved freely by diluted nitric acid. The normal sodic salt  $(\text{NaIO}_3)$  causes, with solutions of normal baric salts, a precipitate of a basic periodate  $2(\text{Ba}_2\text{IO}_4), 3\text{BaO}, 5\text{H}_2\text{O}$ . Analogous precipitates are formed with salts of calcium, of lead, or of silver, whilst the liquid becomes acid. The hydrated argentic basic periodate is pale yellow  $(2\text{AgIO}_4, \text{Ag}_2\text{O}, 3\text{H}_2\text{O})$  if precipitated from cold, but red  $(2\text{AgIO}_4, \text{Ag}_2\text{O}, \text{H}_2\text{O})$  if from hot solutions.

(399) **CHLORIDES OF IODINE.**—Two compounds of iodine with chlorine, a protochloride  $(\text{ICl})$  and a trichloride  $(\text{ICl}_3)$  may be obtained.

The *protochloride*, or *iodous chloride*  $(\text{ICl})$ , is a very irritating, volatile, yellowish-brown liquid, which is obtained by distilling 1 part of iodine with 4 parts of potassic chlorate; the distilled iodous chloride is soluble, apparently without change, in alcohol, and in ether. This chloride when hot dissolves iodine readily, and deposits it in beautiful crystals.

*Trichloride of iodine*, or *iodous trichloride*  $(\text{ICl}_3)$ , is procured by acting upon iodine with excess of dry chlorine gas. It forms magnificent ruby red crystals, which undergo spontaneous sublimation in closed bottles: the vapour is extremely irritating to the eyes. If exposed to the air it attracts moisture, and is dissolved by water without experiencing decomposition. Alkaline solutions decompose it, and iodine is precipitated as in Liebig's method of preparing iodic acid (397).

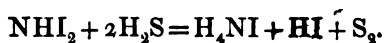
*Bromides of iodine.*—Iodine also combines with bromine, and forms compounds with it which are possessed of properties similar to those of the chlorides of iodine.

(400) **IODIDE OF NITROGEN.**—By digesting iodine for half an hour in a cold solution of ammonia, a black powder is obtained. The brown supernatant liquid, which contains an excess of iodine held in solution by ammoniac iodide, is decanted, and the insoluble powder is placed upon filtering-paper in quantities of a grain or less, and allowed to dry spontaneously. Two com-

pounds ( $\text{NI}_3$  and  $\text{NHI}_2$ ) appear to be formed together under these circumstances; both these compounds, when dry, explode upon the slightest touch, and indeed often detonate without any assignable cause: the explosion is remarkably sharp and sudden, fumes of iodine are produced, and a faint light is emitted.

Stahlschmidt finds that in order to obtain the compound  $\text{NHI}_2$  in a state of purity, a cold saturated solution of iodine in absolute alcohol should be mixed with twice or thrice its bulk of a saturated solution of ammonia in absolute alcohol; the precipitate thus formed must be washed with absolute alcohol. If the alcoholic solution of iodine be precipitated with concentrated aqueous solution of ammonia, and the precipitate washed with water, the black powder consists of a body which may be represented by the formula  $\text{NI}_3$ , or ammonia in which the 3 atoms of hydrogen have been displaced by 3 of iodine.

Iodide of nitrogen becomes slowly decomposed in water; ammonia retards, but potash and the acids accelerate the decomposition; chlorine, bromine, and strong nitric acid destroy it rapidly; sulphuretted hydrogen also effects its decomposition quietly but completely. The results of the reaction last mentioned afford a means of ascertaining the relative quantities of nitrogen and iodine contained in the body under examination: 1 atom of the black powder ( $\text{NHI}_2$ ), when treated with 2 atoms of sulphuretted hydrogen, furnishes 1 atom of ammoniac iodide, 1 of hydriodic acid, and 2 atoms of sulphur;—



(401) *Natural Relations of the Halogens.*—It is impossible not to be struck with the close analogy presented by the three elementary bodies, chlorine, bromine, and iodine, both in their uncombined state and in their compounds: they indeed form one of the best defined natural groups of simple substances. All these elements have the characteristic peculiarity of combining with hydrogen in the proportion of 1 volume of the gas or vapour with 1 volume of hydrogen; the union occurring without change of bulk, and the compound formed being powerfully acid and extremely soluble in water. Chlorine, bromine, and iodine are also capable of displacing hydrogen from many of its organic compounds, producing substances which correspond in composition with the original body, but in which a certain number of atoms of the halogen have taken the place of a corresponding number of atoms of hydrogen.

The specific gravity, fusing-point, and boiling-point of these

elements rise as the atomic weight increases, as is shown in the table which follows :—

Elements.	Sp. gravity.		Melting point.		Boiling point.		Atomic weight.	Diff. between at. weights.
	Gaseous.	Liquid or solid.	°C.	°F.	°C.	°F.		
Fluorine	1·313 <sup>p</sup>	?		<sup>p</sup>		<sup>p</sup>	19	16·5
Chlorine	2·47	1·33		<sup>p</sup>		<sup>p</sup>	35·5	
Bromine	5·54	3·187	—12·5	9·5	63	145·4	80·0	44·5
Iodine	8·716	4·947	107	225·0	175	347·0	127·0	47·0

The intensity of their chemical activity decreases as the combining number increases. At ordinary temperatures, chlorine is gaseous, bromine liquid, iodine solid; the properties of bromine being indeed intermediate between those of chlorine and iodine. When in the liquid form, the three elements have the same atomic volume; and when united with the same metal the salts which they furnish are isomorphous; potassic chloride, bromide, and iodide, for example, all crystallize in cubes. Each of these elements also forms a powerful monobasic acid with 3 and with 4 atoms of oxygen.\* The attraction of these three halogens for oxygen is, however, in the inverse order of that of the same halogens for hydrogen and the metals. Neither iodic anhydride, nor the acid in solution, is decomposed by free chlorine or bromine: bromic acid and the bromates are also unaffected by

Hydrochloric acid. HCl Hypochlorous acid. HClO Chlorous acid. HClO <sub>2</sub> Chloric acid. HClO <sub>3</sub> Perchloric acid. HClO <sub>4</sub>	Hydrobromic acid. HBr Hypobromous acid. HBrO  Bromic acid. HBrO <sub>3</sub> Perbromic acid. HBrO <sub>4</sub>	Hydriodic acid. HI   Iodic acid. HIO <sub>3</sub> Periodic acid. HIO <sub>4</sub>
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free chlorine; but iodic acid is easily obtained by the decomposition of chloric or bromic acid by free iodine, and perbromic acid by acting upon perchloric acid with bromine, though chloric acid is

\* Nitrogen is remotely connected with this group by the similarity of the nitrates with the chlorates, and of the nitrites with the chlorites; it forms an intermediate link in the natural grouping of the elements between the halogens and the elements belonging to the phosphorus family; its compound with hydrogen (viz., ammonia) presenting some analogies with phosphuretted hydrogen, which will be more fully shown hereafter.

only in small proportion converted into bromic acid by the action of bromine upon it. The preceding table exhibits some of the corresponding compounds with hydrogen and oxygen which are formed by the halogens.

At the time that iodine was discovered, chlorine was by most chemists regarded as a compound of muriatic acid and oxygen, and was consequently known as *oxymuriatic acid*. Indeed, many of the reactions which it presented admitted of a simple explanation on this hypothesis, and this circumstance prevented chemists from adopting generally the views which had a short time previously been put forward by Davy, maintaining the elementary nature of chlorine. The discovery of iodine, however, decided them, and assisted materially in fixing the opinion now entertained respecting the compounds of fluorine, the fourth member of the group, and of which our knowledge is in a much less satisfactory condition.

#### § IV. FLUORINE: $F=19$ .

*Theoretical Density*, 1.313; *Comb. Vol.*  $\square$ ; *Rel. wt.* 19;  
*Monad, as in HF.*

(402) MANY unsuccessful attempts have been made at various times to isolate fluorine. Its chemical activity is so powerful, and its action on the human frame is so irritating and deleterious, that little that is satisfactory is known concerning it in its free state. No doubt, however, is entertained of its general nature, since its compounds are closely analogous to the corresponding ones of the three elements which have just been described. According to Kammerer (*Chemisches Centralblatt*, Aug. 1862, p. 523), free fluorine may be obtained in the following manner as a colourless gas which has no action on perfectly dry glass. Into a perfectly dry glass tube iodine is introduced, together with a thin closed glass cylinder containing well-dried argentic fluoride in excess over the iodine. The air must be completely expelled from the tube by converting a portion of the iodine into vapour; the tube is then to be hermetically sealed, and the little cylinder of argentic fluoride broken; after which the tube must be exposed for 24 hours to a temperature of from  $160^{\circ}$  to  $180^{\circ}$  ( $71^{\circ}$  to  $82^{\circ}$  C.). At the end of this time, in an experiment made in this manner, the iodine had entirely disappeared, and a colourless gas, permanent over mercury, and rapidly absorbed by a solution of potash, was obtained.

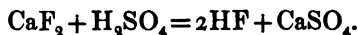
Fluor-spar, or calcic fluoride ( $CaF_2$ ), is, with the exception of cryolite ( $3NaF, AlF_3$ ), the only compound of fluorine which exists



native in abundance; and from it all the preparations of fluorine are obtained. Small quantities of calcic fluoride are contained in a variety of minerals, particularly in the phosphates of calcium and certain kinds of mica. It exists too in minute quantity in the bones of animals, and especially in the teeth.

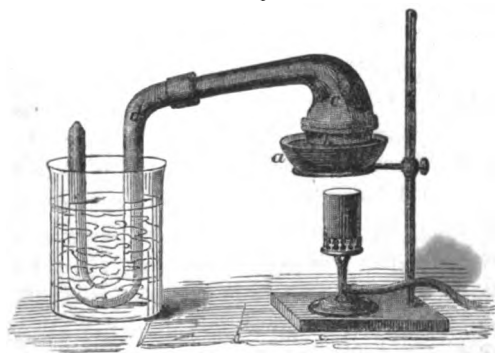
(403) HYDROFLUORIC ACID: *Hydric fluoride* ( $\text{HF} = 20$ ); *Rel. wt.* 10; *Theoretic Sp. Gr. of anhydrous Vapour*, 0.689; *Atomic Vol.*   .—Fluorine is not known to form any oxide, but with hydrogen it constitutes a very remarkable acid.

*Preparation.*—In order to procure hydrofluoric acid in solution in a concentrated form, 1 part of finely powdered fluor-spar, free from silica and the metallic sulphides, is mixed with 2 or 3 parts of oil of vitriol; at ordinary temperatures no evolution of vapour occurs if the fluor-spar be pure, but a transparent gelatinous mass is formed. On the application of a gentle heat dense acid fumes of an extremely deleterious nature arise, and a reaction takes place similar to that which occurs in the preparation of hydrochloric acid; for instance,



Owing to the powerfully corrosive action exerted by hydrofluoric acid upon glass, which it deprives of its silicon, it is necessary always to prepare it in metallic vessels. For ordinary purposes, the distillation may be conducted in a leaden retort. For

FIG. 310.



the convenience of removing the charge after the operation is over, it is found advantageous to make the retort in two pieces, a head and a body; the head, *c*, fig. 310, fits accurately by an overlapping grooved joint into the body, *b*. The heat may be conveniently

applied in an equable manner by placing the body of the retort in a shallow iron tray, *a*, filled with sand: *d* is the receiver for the acid: it consists of a leaden pipe fitted by grinding to the neck of the retort, and is cooled by immersion in a mixture of ice and salt. When a perfectly pure acid is required, the still and receiver must consist of platinum.

The concentrated acid obtained by the foregoing method was long believed to be anhydrous; but the researches of Louyet (*Comptes Rendus*, xxiv. 434) have proved that it contains water. He distilled it with an excess of phosphoric anhydride: the water was thereby removed, and a colourless gas of an extremely irritating nature was set free: it produced dense fumes on escaping into the air, had but little action on perfectly dry glass, and was rapidly condensed by water. Fremy (*Ann. de Chimie*, III. xlvii. 7) prefers to subject the double fluoride of potassium and hydrogen (KF, HF) to distillation; the salt is first rendered anhydrous by careful desiccation, and by afterwards applying a strong heat, the equivalent of hydrofluoric acid is expelled: by the application of a freezing mixture of ice and salt, the anhydrous acid is said to be obtained in the form of a colourless, mobile, very volatile liquid. Fremy also obtained the anhydrous acid by decomposing plumbic fluoride by dry hydrogen.

**Properties.**—The acid obtained by distilling fluor-spar with oil of vitriol is a densely fuming, volatile, colourless liquid, which boils at about  $60^{\circ}$ , and remains unfrozen at  $-4^{\circ}$  ( $-20^{\circ}$  C.). The preparation of this acid must be conducted with the greatest care, and special provision must be made for carrying off the fumes from the operator. The liquid acid is highly dangerous, from its caustic action upon the skin; the smallest drop occasioning a deep and painful burn. Indeed, it ought never to be preserved in the concentrated form. When poured into water it combines with it with great avidity, and with the evolution of so high a temperature as to produce a hissing noise, resembling that caused by quenching a red-hot iron. In its concentrated form it has a specific gravity of 1.060, but by the addition of water the density may be increased to 1.150, beyond which point further dilution is attended with a regular decrease in density. The acid of sp. gr. 1.150 ( $\text{HF}, 2\text{H}_2\text{O}$ ), boils at  $248^{\circ}$  ( $120^{\circ}$  C.), and may be distilled unchanged. (See note p. 152.) Diluted hydrofluoric acid gradually dissolves the metals, excepting platinum and some of the metals associated with it, and gold, silver, lead, and mercury; the metal whilst undergoing solution displaces hydrogen. Potassium, if thrown into the strong acid, decomposes it with explosion.

**Tests.**—Hydrofluoric acid is easily recognized by its corrosive action upon glass. In order to detect a fluoride in a compound which is suspected to contain it, the material is reduced to a fine powder and mixed in a platinum capsule with strong sulphuric acid; a slip of glass is warmed and rubbed over with bees'-wax so as to coat it uniformly; a few characters are next traced with

a point through the wax, so as to expose a portion of the glass: this etching is then inverted over the platinum capsule, which is gently warmed for a few minutes, the glass being cooled with a piece of moistened filtering paper, in order to prevent the wax from becoming melted. If fluorine be contained in the mixture, the glass, on cleaning off the wax with a little oil of turpentine, will be found to be corroded in the parts exposed: if the traces be very faint, they may be rendered visible by breathing upon the surface of the plate.

A weak solution of hydrofluoric acid is often employed advantageously for etching on glass: in this way, for instance, the graduations on the glass stem of a thermometer may be made with great precision and facility; the glass tube is first coated with engravers' etching varnish, the divisions are traced through the varnish with a fine point, and the tube is plunged into a long leaden tube filled with the diluted acid; in the course of a few minutes the scale is permanently engraved: when the engraving is effected by the vapour of the acid, the traces are white and opaque, but if the liquid acid be used the lines are transparent.

*Fluorides.*—The compounds of the metals with fluorine for the most part fuse easily on the application of heat, and hence the origin of the terms *fluor-spar* and fluorine (from *fluo*, to flow). When ignited in a current of steam many of them are converted into the corresponding oxide, whilst hydrofluoric acid is formed. A large number of the fluorides are insoluble, or only sparingly soluble, in water. They are all decomposed when heated with oil of vitriol, and evolve hydrofluoric acid; but they are not so readily attacked by nitric acid. If heated with chlorine, many of the fluorides are decomposed, whilst chlorides of the metal are produced. The solutions of the soluble fluorides corrode the glass vessels in which they are contained: they give no precipitate with argentic nitrate, since argentic fluoride is soluble; but with salts of lead, barium, magnesium, and calcium, insoluble precipitates, consisting of the fluorides of these metals, are produced. Calcic fluoride is so transparent as to be perceived with difficulty; but on heating the liquid, or on the addition of ammonia, it is rendered more opaque.

Many metallic fluorides combine with an additional atom of hydrofluoric acid, and form compounds which may often be obtained in crystals that are soluble in water. The double fluoride of potassium and hydrogen ( $\text{KF}, \text{HF}$ ) has been already mentioned as a convenient source of concentrated hydrofluoric acid. Double fluorides of the alkali-metals with the fluorides of the electro-

negative metals which form acids with oxygen may likewise be obtained with facility. Many insoluble metallic anhydrides, such as the tantalic, titanic, molybdic, and tungstic anhydrides, are thus dissolved by hydrofluoric acid, fluorides of the metals being formed, whilst the oxygen of these compounds produces water with the hydrogen of the hydrofluoric acid: the metallic fluorides so formed are dissolved by the excess of hydrofluoric acid, and give rise to new compound acids. Titanic anhydride, for instance, is thus converted into fluotitanic acid;  $\text{TiO}_2 + 6\text{HF}$  becoming  $(2\text{HF}, \text{TiF}_4) + 2\text{H}_2\text{O}$ . Silica yields a similar compound  $(2\text{HF}, \text{SiF}_4)$ .

Hydrofluoric acid, when mixed with nitric acid, readily dissolves silicon which has not been strongly ignited; but it is remarkable that the mixture does not dissolve either gold or platinum.

Numerous other compounds of fluorine have been prepared, but they are not of sufficient practical importance to require notice here: the compounds which it forms with silicon and with boron will be described hereafter (478, 483).

(404) *Determination of the Combining Proportion of Fluorine.*—Although the chemist has hitherto been unable to isolate fluorine in a state of purity, yet its combining proportion has been determined with precision; and the mode of proceeding offers an instructive illustration of the resources of chemical analysis in such a case.

The method of operating is as follows:—Pure fluor-spar is reduced to an impalpable powder, and dried; 10 grms. of this powder are accurately weighed into a counterpoised platinum crucible, and concentrated sulphuric acid, also perfectly pure, is added in quantity sufficient to reduce the whole to the consistence of cream: after standing for some hours, the excess of acid is expelled by the heat of a lamp: the temperature is raised very cautiously, and the crucible and its contents are finally heated to bright redness. In this operation the whole of the fluorine unites with the hydrogen and is expelled in the form of hydrofluoric acid, whilst the calcium combines with sulphurion, and forms calcic sulphate, which remains behind. On weighing the crucible after the experiment is completed, the calcic sulphate will be found to amount to 17·436 grammes.

Now it is known that 68 parts of calcic sulphate contain 20 of calcium and 48 of sulphurion, 20 being the quantity of calcium equivalent to one atom of hydrogen, ( $\text{H} = 1$ ) though since it is a dyad its atomic weight is 40 (13):—

$$\text{but } 68 : 20 :: 17\cdot436 : x (= 5\cdot125);$$

17·436 grms. of calcic sulphate must consequently contain 5·125 of calcium; 100 parts, therefore, of fluor-spar, if it consist only of fluorine and calcium, must be composed of 51·25 of calcium and 48·75 of fluorine. The combining proportion of fluorine is then found directly by the following calculation:—

Qty. of calcium in 100 parts.	Equiv. of calcium.	Qty. of fluorine in 100 parts.	Equiv. of fluorine.
51·25	: 20	: 48·75	: 19.

The quantity of fluorine equivalent to 1 atom of hydrogen is thus ascertained to be 19.

## CHAPTER VII.

## SULPHUR—SELENIUM—TELLURIUM.

(405) *Natural Relations of the Sulphur Group.*—Between sulphur, selenium, and tellurium, a marked analogy in chemical character is observable. They are all characterized by a powerful attraction for oxygen. The properties of selenium are intermediate between those of sulphur and tellurium, which latter presents so much the external characters and appearance of a metal, that it is usually described with the metals. The specific gravity and fusing-point of these elements increase as the atomic weight increases, as will be seen by comparing the numbers in the different cases :—

Elements.	Specific gravity.	Melting point.		Boiling point.		At. wt.	Difference between at. wts.
		°C.	°F.	°C.	°F.		
Sulphur ...	2.05	115	239	446	836	32	47.5
Selenium ...	4.788	217	423			79.5	49.5
Tellurium ...	6.65	482	900			129	

Amongst the compounds of each of these bodies with oxygen are two anhydrides ; one with 2 atoms of oxygen corresponding with sulphurous anhydride  $\text{SO}_2$ , and another with 3 atoms of oxygen corresponding with sulphuric anhydride  $\text{SO}_3$ . One volume of the vapour of each of these three elements unites with 2 volumes of hydrogen to form 2 volumes of a sparingly soluble gaseous compound possessed of a disgusting odour and feebly acid character. Oxygen also presents a certain analogy with the members of this group, 1 volume of oxygen uniting with 2 volumes of hydrogen to form 2 volumes of steam ; and the oxides and sulphides, generally, exhibit many points of resemblance. In general the members of this group exhibit dyad functions, though in some cases they act as tetrads, sulphur forming a compound with four atoms of ethyl,  $\text{S}(\text{C}_2\text{H}_5)_4$ , and selenium and tellurium, each combining with 4 atoms of chlorine.

The atomic volume of solid sulphur is 101, and that of selenium 103, or nearly identical ; but that of tellurium, 128, is one-fourth higher. It may be further remarked that the corresponding compounds of sulphur, selenium and tellurium are isomorphous.

The singular numerical relations which Dumas and others

have pointed out between the atomic weights of the members composing these groups and those of several other elements equally closely allied, will be discussed at a future point.

It will be sufficient here to remark, that in groups of electro-negative elements of similar properties it is usually observable that the chemical activity of each element of the group is usually greater, the smaller is its combining number; sulphur, for example, being more active in its chemical relations than selenium, and selenium than tellurium: so again, fluorine is more energetic in its chemical actions than chlorine, chlorine than bromine, and bromine than iodine. In the metallic, or basylous elements, the order of their activity is exactly the reverse, potassium being more active than sodium, and sodium than lithium.

The following table exhibits some of the corresponding compounds which the elements of this group form with oxygen and hydrogen:—

Water. $\text{H}_2\text{O}$	Sulphuretted hydrogen. $\text{H}_2\text{S}$ Sulphurous acid. $\text{H}_2\text{SO}_3$ Sulphuric acid. $\text{H}_2\text{SO}_4$	Seleniuretted hydrogen. $\text{H}_2\text{Se}$ Selenious acid. $\text{H}_2\text{SeO}_3$ Selenic acid. $\text{H}_2\text{SeO}_4$	Telliuretted hydrogen. $\text{H}_2\text{Te}$ Tellurous acid. $\text{H}_2\text{TeO}_3$ Telluric acid. $\text{H}_2\text{TeO}_4$
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### § I. SULPHUR : S=32.

*Combining Volume below*  $1500^\circ$  ( $815^\circ$  C.)  $\frac{1}{2}$ ; *above*  $1904^\circ$  ( $1040^\circ$  C.)

$\square$ ; *Rel. wt.* 32; *Observed Specific Gravity of Vapour at*

$1904^\circ$ , 2.23, *at*  $900^\circ$  ( $482^\circ$  C.), 6.617; *Theoretic Sp. Gr.*

*at*  $1904^\circ$ , 2.2168. *Melting-pt.*  $239^\circ$  ( $115^\circ$  C.); *Boil-*

*ing-pt.*  $836^\circ$  ( $446^\circ$  C.); *Dyad, as in*  $\text{H}_2\text{S}$ ; *Mol.*

*vol. of vapour* (SS) =  $\square$ ; *Mol. wt.* = 64.

(406) Most of the sulphur used in England is obtained from Sicily, where it occurs in the native or uncombined state in beds of a blue clay formation, stretching from the southern coast of the island towards the base of Mount Etna. It is also found abundantly in volcanic districts generally, and particularly in those which border the Mediterranean. Many of the compounds of sulphur with the metals occur in great abundance as natural productions,—especially the sulphides of iron, copper, lead, and zinc. Ferric disulphide ( $\text{FeS}_2$ , iron pyrites) furnishes a large proportion of the sulphur consumed in the manufacture of oil of

vitriol. Sulphur is still more extensively distributed in the oxidized condition as sulphuric acid, in combination with various earths; the sulphates of calcium, magnesium, barium, and strontium being abundant natural productions. Sulphur is likewise an essential constituent of many bodies of organic origin; it enters into the composition of several foetid volatile oils; it is a necessary ingredient in the muscular tissue of animals, and is indeed, always contained in the albuminoid or proteic compounds.

*Properties.*—Native sulphur is found either in amorphous masses, or in transparent yellow crystals, the form of which is derived from the octohedron with a rhombic base. The sulphur of commerce is presented either as a harsh, yellow, gritty powder, known as *flowers of sulphur*, or in round sticks, constituting roll sulphur or common *brimstone*. In the latter condition it is a solid, nearly opaque, brittle substance, of a characteristic yellow colour, with a slight, peculiar odour. It is insoluble in water, and is consequently tasteless; it is a bad conductor of heat, and when grasped with a warm hand frequently crackles and falls to pieces from the unequal expansion; it is an insulator of electricity, and becomes negatively electric by friction.

Sulphur is highly inflammable, and when heated in the air it takes fire at between  $455^{\circ}$  and  $500^{\circ}$  ( $235^{\circ}$  and  $260^{\circ}$  C.), burning with a blue flame, and emitting pungent suffocating fumes of sulphurous anhydride. At  $239^{\circ}$  ( $115^{\circ}$  C.) it melts, forming a yellow liquid which is less dense than the unmelted sulphur. In closed vessels it may, by a further heat, be distilled, the boiling-point being about  $836^{\circ}$  ( $446^{\circ}$  C.) (Regnault); at this temperature sulphur yields a deep yellow vapour of sp. gr. 6.617: 1 volume of this vapour contains 3 atoms of sulphur. Bineau found that when sulphur is heated to about  $1832^{\circ}$  ( $1000^{\circ}$  C.), the vapour becomes dilated to three times the bulk that an equal weight of the vapour occupies at  $900^{\circ}$  ( $482^{\circ}$  C.), and that at this high temperature the volume occupied by an atom of sulphur vapour corresponds with that of an atom of oxygen; this observation has recently been confirmed by Deville and Debray.

Sulphur combines readily with chlorine, with bromine, and with iodine, especially when the action is favoured by heat. It also enters rapidly into combination with most of the metals, many of which, like copper, iron, and silver, if in a state of fine division, burn vividly when heated in its vapour. The compounds of sulphur with the metals are now termed *sulphides*, formerly they were known as *sulphurets*. Generally for each sulphide a corresponding oxide exists, each atom of oxygen in the molecule

of the oxide being represented in the sulphide by an atom of sulphur; and sulphur often displaces oxygen by double decomposition; 1 atom of sulphur is therefore equivalent to 1 atom of oxygen and to 2 atoms of hydrogen or of chlorine.

*Extraction.*—When the proportion of sulphur in the matrix is large, the earthy impurities are removed by simply melting out the sulphur from them; but when the proportion of sulphur does not exceed 8 or 12 per cent. it is found to be more advantageous to subject the mineral to a rough distillation, which is performed upon the spot where it is obtained. For this purpose a long brick furnace is constructed so as to contain a double row of upright earthenware retorts, each of a capacity of 4 or 5 gallons (18 or 22 litres): each retort is furnished with a large aperture at the top for charging it with the sulphur, and with a short wide tube, which proceeds from the side at the upper part, and slopes downwards through the walls of the furnace into an earthen receiver of a form similar to that of the retort: from the bottom of the receiver a short pipe carries off the still melted sulphur into a vessel containing water. It is, however, yet very impure, and requires a second more careful distillation before it is fit for many of the purposes to which it is applied in the arts. This second distillation is conducted in retorts, generally of iron, furnished with a short, wide, lateral neck; the fumes are received into large chambers of brickwork. If the walls of these chambers be kept cool, and the process be conducted slowly, the sulphur is condensed in powder, and forms 'flowers of sulphur'; but if the fire be urged, and the masonry be allowed to become hot, the sulphur melts, runs down, and is then drawn off into cylindrical wooden moulds, which give it the usual form of roll sulphur.

When sulphur is prepared from pyrites ( $\text{FeS}_2$ ), the mineral is sometimes distilled in closed vessels, and by this means about one-third of the sulphur which it contains is volatilized and condensed, magnetic pyrites,  $\text{Fe}_3\text{S}_4$ , remaining; but it is more usual to conduct the operation in the open air, as a preliminary step in the roasting of copper pyrites to prepare it for smelting. Huge heaps of the ore are arranged in the form of a truncated square pyramid, the base of which is about 30 feet (or 10 metres) in the side. A layer of powdered ore is placed at the bottom, and over this one of brushwood; in the centre is constructed a wooden chimney, which communicates with air-ways left between the fagots; fragments of ore are now piled up until the heap is about 8 feet (2·5 metres) high, and lastly the whole is covered, for a depth of 12 inches (30 centimetres), with a layer of powdered ore. Such a heap contains upwards of 2000 tons of pyrites, and will furnish about 20 tons of sulphur. When the construction of the heap is complete, the fire is kindled in the centre by dropping lighted fagots down the chimney; in the course of a few days the heat becomes diffused throughout the mass, and sulphur begins to ooze from the surface. When this is observed, numerous hemispherical wells or excavations, fitted with covers, are made in the superficial layer of ore, for the reception of the sulphur; into these cavities it drains, and is daily ladled out and cast into moulds. The process of roasting such a heap occupies five or six months.

*Uses.*—Sulphur is extensively employed in the arts; from its ready inflammability it is used to facilitate the combustion of many bodies, as in the preparation of matches; and large quantities are consumed in the manufacture of gunpowder. It is employed to some extent as a medicine, especially in certain forms of cutaneous disease; when converted into sulphurous acid it is



applied to the bleaching of silks and flannels; but its chief consumption is in the production of sulphuric acid.

(407) *Various forms of Sulphur*.—Sulphur has been already pointed out (87) as affording a striking illustration of the occurrence of allotropy: it may be obtained in several distinct modifications of form, or in different allotropic states.

The first form is the native crystal of sulphur, the octohedron with a rhombic base. It may be obtained artificially by allowing the solution of sulphur, in chloride of sulphur, or in carbonic disulphide, to evaporate spontaneously. It is semi-transparent, of an amber yellow colour, and has a density of 2.05. Its crystals undergo no change in the air: they fuse at  $239^{\circ}$  ( $115^{\circ}$  C.).

The second variety is obtained by melting 2 or 3 kilogrammes of sulphur, and allowing it to solidify on the surface; if the crust be pierced with a hot wire, the still fluid portion may be poured off, and the solid mass beneath will be found to be lined with transparent brownish-yellow needles, belonging to the oblique prismatic form; these have a specific gravity considerably less than octohedral sulphur, viz., 1.98, the density of ordinary roll sulphur. According to Brodie, it melts at  $248^{\circ}$  ( $120^{\circ}$  C.). This form is not permanent in the air: in a few days, or (if the surface of the crystals be scratched) in a few hours, the transparency disappears, and although to the eye the crystals retain their prismatic outline, they lose their coherence, and an opaque crumbling mass is produced, consisting of minute rhombic octohedra. On the other hand, if an octohedron of sulphur be placed in a liquid, the temperature of which is slowly raised to a point between  $220^{\circ}$  and  $230^{\circ}$  ( $104^{\circ}$  and  $110^{\circ}$  C.), it loses its transparency, owing to the formation of prismatic crystals.

Mitscherlich has ascertained that in the passage of the prismatic into the octohedral form, an amount of heat is emitted which would raise the temperature of an equal weight of water  $4^{\circ}.09$  ( $2^{\circ}.27$  C.). This conversion of the prismatic into the octohedral variety may be effected suddenly, by immersing the prisms in a solution of carbonic disulphide, even when this solvent is already saturated with sulphur (*Ann. de Chimie*, III. xlv. 124).

The third variety is even more remarkable than the preceding forms: it is produced by the action of a still higher temperature. The influence of heat upon sulphur is indeed very peculiar. It begins to melt at about  $239^{\circ}$  ( $115^{\circ}$  C.), and between  $248^{\circ}$  ( $120^{\circ}$  C.) and  $284^{\circ}$  ( $140^{\circ}$  C.) it forms a yellow, transparent, and tolerably limpid liquid: as the temperature rises, the colour deepens, it becomes brown, and at last nearly black and opaque. At  $356^{\circ}$

(180° C.) these changes are very decided ; it gradually becomes more and more viscid ; the temperature at this point for a while becomes stationary, notwithstanding continued accessions of heat from without, so that heat is becoming latent, as in the analogous case of the melting of ice. After a while, if the application of heat be steadily continued, the temperature again rises, and when it has attained to nearly 500° (260° C.) the sulphur once more liquefies, though it never becomes as fluid as at the temperature of 248° (120° C.) when first melted. If it be now suddenly cooled by pouring it in a slender stream into cold water, a soft tenacious mass is produced, which may be drawn out into elastic threads. The colour of the cooled threads varies from a pale amber to a deep brown, becoming darker in proportion to the elevation of temperature which it has experienced. Magnus has shown (*Pogg. Annal.* xcii. 308) that this deepening in colour of the melted sulphur is due to the formation of another modification of sulphur, which is black ; the more frequently the sulphur is heated up to about 599° (315° C.), and then suddenly cooled, the larger is the quantity of this black sulphur which is formed : the details of the process required for insulating it are given at length in the memoir above referred to. A red variety of sulphur was also obtained by Magnus, which Mitscherlich proved to be produced only when a minute quantity of some fatty body is present. Ductile sulphur has a sp. gr. of only 1.957. In a few hours it becomes yellow and opaque, and returns to the brittle form, giving out again the heat which it had absorbed ; it also increases in density, the greater part of it assuming the octohedral form. If this ductile sulphur be heated to 212°, it suddenly returns to the brittle condition, the temperature rising to 230° (110° C.) during the change.

(408) According to Berthelot (*Ann. de Chimie*, III. xlix. 435) there are among the various modifications of which sulphur is susceptible, two principal forms which are more stable than the rest. These are the *octohedral*, or, as he terms it, the *electro-negative* variety, the most permanent condition of sulphur, and a pulverulent, or *electropositive* form, which is insoluble in carbonic disulphide.

In the so-called electronegative or octohedral condition sulphur is soluble in carbonic disulphide. This variety is deposited at the positive electrode of the voltaic battery during the electrolysis of an aqueous solution of sulphuretted hydrogen. To this variety, the prismatic form, and the white precipitate obtained from the alkaline polysulphides by the addition of an acid, also belong. It is this form which is always deposited from cold solutions of sulphur ; whether the solvent be alcohol, benzol, carbonic disulphide, or chloride of sulphur.

The electropositive condition is obtained when sulphur is separated from its combinations with elements which, like oxygen, bromine, and chlorine, are more electronegative than sulphur itself. The most stable variety is that obtained by treating flowers of sulphur first with carbonic disulphide, then with alcohol, and then a second time with the disulphide; it is somewhat less stable when procured from the chloride of sulphur by decomposing it with water; if the precipitate thus occasioned be purified by digestion in carbonic disulphide, a yellow, or orange-yellow, amorphous powder is procured. This amorphous sulphur is much more readily oxidized when heated with nitric acid than the crystalline modification. If maintained at  $230^{\circ}$  ( $110^{\circ}$  C.) for some time, it gradually passes into the octohedral modification, evolving heat during the change. If amorphous sulphur be heated to  $572^{\circ}$  ( $300^{\circ}$  C.), then suffered to cool very slowly, and submitted to 2 or 3 successive sublimations at a low temperature, it becomes converted into the electronegative condition, and is rendered entirely soluble in carbonic disulphide. The electropositive variety may also be slowly converted into the electronegative form by contact with certain electropositive substances, as by digestion for some days in a solution of liquid ammonia, in one of disodic sulphide, or in one of hydropotassic sulphite ( $\text{KHSO}_3$ ), in which case a portion of the sulphur becomes dissolved, and the remainder is rendered soluble in carbonic disulphide. Electropositive sulphur is deposited at the negative electrode of the battery during the electrolysis of sulphurous or sulphuric acid. Other modifications of the insoluble form of sulphur, which pass with greater facility than the foregoing one into the soluble variety (for example, by exposure to  $212^{\circ}$  for some hours), may be obtained by decomposing the oxidized compounds of sulphur, such as the hyposulphites, by acids. The black sulphur of Magnus is also insoluble in carbonic disulphide.

Crystalline sulphur, of either the octohedral or the prismatic form, is soluble in about 3 times its weight of carbonic disulphide; it is also dissolved freely by the chloride of sulphur; by spontaneous evaporation of these liquids, the sulphur is left in octohedra. Benzol is also an excellent solvent for sulphur, especially when heated. Boiling oil of turpentine likewise dissolves sulphur freely, and retains 1.5 per cent. of it on cooling: as the liquid cools, the sulphur crystallizes, first in the prismatic form, afterwards, as the temperature continues to fall, octohedra are produced. Vitreous sulphur is but partially soluble in carbonic disulphide; and after it has lost its vitreous and tenacious character by exposure to the air, it is not wholly changed into the crystalline form of sulphur, for when treated with carbonic disulphide a pale buff-coloured powder of sp. gr. 1.955 is left; it may, by fusion, be reconverted into ordinary sulphur, soluble in carbonic disulphide. If vitreous sulphur be left in contact for 24 hours with an aqueous solution of sulphuretted hydrogen, it is changed into the amorphous form.

All the varieties of sulphur are soluble to a small extent in boiling anhydrous alcohol, the electropositive varieties becoming modified as they are dissolved: the hot solution as it cools deposits minute transparent prismatic crystals of the electronega-

tive variety. Chloroform and ether dissolve sulphur less freely than alcohol.

When sulphur is distilled in small quantities, and received into vessels in which the temperature is not considerably reduced, the sulphur is condensed in red drops, which remain liquid for many hours. Sulphur is also frequently liberated in the ductile form from the native sulphides of the metals during their solution in *aqua regia*, and from the hyposulphites when decomposed by concentrated hydrochloric acid. When nitric acid is used, the sulphur is separated in solid flocculi.

(409) COMPOUNDS OF SULPHUR WITH OXYGEN.—Two oxides only of sulphur are known in the anhydrous state, viz.:—

	Mol. wt.	Mol. vol.	Sulphur.	Oxygen.
Sulphurous anhydride $\text{SO}_2$	= 64	<input type="text"/>	50'00	+ 50'00 = 100
Sulphuric anhydride $\text{SO}_3$	= 80	<input type="text"/>	40'00	+ 60'00 = 100

Sulphur, however, forms numerous oxidized acid compounds: two of them (sulphurous acid and sulphuric acid) have been long known and employed on a large scale in the arts; the others are less important, and of comparatively recent discovery. Some of these acids of sulphur are interesting, inasmuch as they exhibit a combining ratio different from any which we have as yet considered, and they show the application of the law of multiple proportions to the case of the sulphur, as well as to that of the oxygen which they contain.

The following table exhibits the composition of the various oxyacids of sulphur, the existence of which is at present known. The five compounds which stand last on the list are often spoken of as constituting the *polythionic* series (from  $\pi\omicron\lambda\upsilon$ , many,  $\theta\epsilon\iota\omicron\nu$ , sulphur), in allusion to the multiple proportion in which the sulphur enters their composition:—

Sulphurous acid	...	...	...	$\text{H}_2\text{SO}_2$	= 82
Sulphuric acid	...	...	...	$\text{H}_2\text{SO}_4$	= 98
Hyposulphurous acid	...	...	...	$\text{H}_2\text{S}_2\text{H}_2\text{O}_4$	= 132
Dithionic	"	...	...	$\text{H}_2\text{S}_2\text{O}_6$	= 162
Trithionic	"	...	...	$\text{H}_2\text{S}_3\text{O}_6$	= 194
Tetrathionic	"	...	...	$\text{H}_2\text{S}_4\text{O}_6$	= 226
Pentathionic	"	...	...	$\text{H}_2\text{S}_5\text{O}_6$	= 258

We will examine first the sulphurous acid, then the sulphuric acid, and will pass slightly over the other acids, the compounds of which, with the exception of some of the hyposulphites, have as yet received no practical applications.

(410) SULPHUROUS ANHYDRIDE (formerly *Sulphurous Acid*):  $\text{SO}_2$ , 64; Mol. Vol. ; Rel. wt. 32; Theoretic Sp. Gr. of

*Gas*, 2.2112; *Observed*, 2.247; *of Liquid*, 1.38, at 60° (15° C.); *Melting-pt.* —105° (—76° C.); *Boiling-pt.* 14° (—10° C.).—Sulphur burns in oxygen with a lilac-coloured flame, and produces a permanent gas; after the combustion has terminated, and the gas has been allowed to regain its original temperature, the bulk of the gaseous products is found to be the same as before the experiment, but the density of the gas is doubled. This experiment furnishes an easy proof of the composition of the gas; for it is thus shown to contain equal weights of sulphur and oxygen. Sulphurous anhydride is the sole product if the oxygen be dry.

The composition of sulphurous anhydride may be represented in the following way:—

			By weight.		By vol.		Sp. gr.
Sulphur ...	S	=	32	or 50	1	or 0.5	= 1.1056
Oxygen ...	O <sub>2</sub>	=	32	50	2	1.0	= 1.1056
<hr/>			<hr/>	<hr/>	<hr/>	<hr/>	
Sulphurous anhydride }	SO <sub>2</sub>		64	100	2	1.0	= 2.2112

*Properties.*—This gas has a pungent suffocating odour, like that of burning sulphur, and in a concentrated form it is quite irrespirable; but if breathed in a diluted form it produces the symptoms of ordinary catarrh. It is not inflammable, but quickly extinguishes the flame of burning bodies. Sulphurous anhydride combines with water immediately, and becomes converted into *sulphurous acid*, H<sub>2</sub>SO<sub>3</sub>. This compound has never been isolated in a pure state, and a very gentle heat is sufficient to occasion the decomposition of its solution into the anhydride and water. The liquid has a taste and smell similar to that of the gas; the solution gradually absorbs oxygen from the air, and becomes converted into sulphuric acid. A crystalline hydrate of sulphurous acid (SO<sub>2</sub>.15H<sub>2</sub>O, Schönfeld; or SO<sub>2</sub>.9H<sub>2</sub>O, Pierre) may also be obtained at a low temperature: at 39° (4° C.) this hydrate melts and is decomposed. Water, according to Bunsen, takes up, at 32°, 68.8 times its bulk of the gas; 43.5 times its bulk at 59° (15° C.); and 32 at 75° (24° C.). Owing to the solubility of sulphurous anhydride in water, the gas must always be collected either over mercury, or in dry bottles by displacement: from the high density of the gas (double that of oxygen), the latter method is easily applied.

*Preparation.*—1. When required in a pure state, sulphurous anhydride is always prepared by depriving oil of vitriol of part of its oxygen. In order to effect this, two or three ounces (about 90 grammes) of sulphuric acid in a concentrated form may be boiled in a glass retort upon half an ounce (15 grms.) of copper

clippings or of mercury. The result of the reaction in the case of copper is indicated by the following equation :—



The gas must be washed by allowing it to bubble up through a bottle containing a small quantity of water, which retains sulphuric acid and any impurities which might be mechanically suspended in the gas.\*

2.—Sulphuric acid may be more economically deoxidized by means of charcoal or dry sawdust, but the gas in this case is accompanied by one-half its volume of carbonic anhydride;  $\text{C} + 2\text{H}_2\text{SO}_4 = 2\text{SO}_2 + \text{CO}_2 + 2\text{H}_2\text{O}$ . For most purposes, however, such as the preparation of the alkaline sulphites, the presence of carbonic anhydride is unimportant.

3.—Sulphurous anhydride may also be procured readily by a process of oxidation: for example, by heating in a flask an intimate mixture of 4 parts of flowers of sulphur and 5 of finely powdered peroxide of manganese, sulphurous anhydride and manganous sulphide are produced;  $\text{S}_2 + \text{MnO}_2 = \text{SO}_2 + \text{MnS}$ . A result somewhat similar is obtained by heating a mixture of 3 parts of cupric oxide with 1 part of sulphur;  $2\text{CuO} + \text{S}_2$  becoming  $\text{Cu}_2\text{S} + \text{SO}_2$ .

Sulphurous anhydride is emitted abundantly from the craters of volcanoes, and it is occasionally met with in solution in the springs of volcanic districts.

Sulphurous anhydride, by transmission through a tube surrounded by a mixture of ice and salt, may be condensed to a colourless, transparent, limpid liquid, which dissolves bitumen; it freezes at  $-105^\circ$  ( $-76^\circ \text{C.}$ ), forming a transparent, colourless, crystalline solid, heavier than the liquid; in closed tubes, at  $60^\circ$  ( $15^\circ\cdot5 \text{C.}$ ) it exerts a pressure of 2·54 atmospheres. Fig. 311 shows a method of liquefying sulphurous anhydride. The gas is generated in the flask, A, washed and dried by means of concentrated sulphuric acid placed in the bottle, B, transmitted through the pewter worm, C, which is surrounded by a freezing mixture of ice and salt, and collected in the receiver, D, which is also cooled by a freezing mixture; the liquefied compound is stored up for use in small tubes, one of which is shown at E, fig. 312: the tube having been placed in the freezing mixture, the anhydride is poured into it through a small tube funnel, and the liquid is preserved by drawing off and sealing the tube at the narrow portion in the flame of the blowpipe, whilst the receiver still remains in the freezing mixture.

*Uses.*—Sulphurous acid possesses considerable bleaching powers, and is extensively employed in bleaching straw and wool,

\* According to Maumené, a certain quantity of cupreous sulphide,  $\text{Cu}_2\text{S}$ , is also produced during this operation, after which a mixture of cupric sulphide and oxy-sulphide is also formed. In this insoluble residue, according to Millon and Commaille, every trace of arsenic in the sulphuric acid, or in the copper dissolved, accumulates.

as well as silken goods, isinglass, sponge, and other articles which would be injured by chlorine. The articles to be bleached are

FIG. 311.

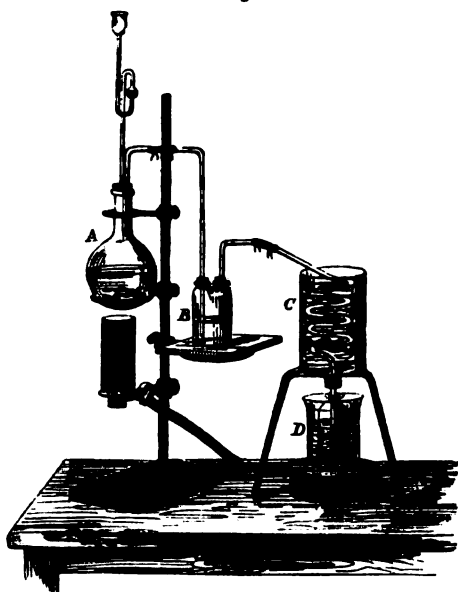


FIG. 312.



moistened, and suspended in closed chambers in which sulphur is burned in an open dish; the sulphurous anhydride is absorbed by the damp goods, and their colour is discharged. The acid appears to act by forming colourless compounds with certain colouring matters. It does not, like chlorine, decompose the colouring matter; for the sulphurous acid may either be expelled by a stronger acid, or it may be neutralized by an alkali, and the colour will be restored: the reproduction of the yellow colour in new flannel, when it is washed with an alkaline soap for the first time, affords a practical illustration of the effect of an alkali upon goods which have been bleached by sulphurous acid. Sulphurous anhydride is also highly valuable as a disinfecting agent. It is a powerful antiseptic. Meat which has been exposed to the action of the gas, and then sealed up in metallic canisters filled with nitrogen to which a little nitric oxide has been added to remove the last traces of oxygen, may be preserved fresh for years. It is often used to check fermentation in cider, or in home-made wine: a little sulphur being burned in the cask before filling it with the liquor.

It is, however, principally as a preliminary step in the manufacture of oil of vitriol that sulphurous anhydride is made upon

the large scale, and in this case it is always obtained by burning sulphur, or a metallic sulphide, in air.

(411) *Sulphites*.—Sulphurous acid is a weak dibasic acid. With the alkalis it forms two kinds of salts, one of which is represented by the ordinary disodic sulphite ( $\text{Na}_2\text{SO}_3 \cdot 10\text{H}_2\text{O}$ ), while the other class is represented by the hydro-potassic sulphite ( $\text{KHSO}_3$ ) often called the bisulphite. The sulphites of the alkali-metals are the only ones which are freely soluble in water; but those of barium, strontium, and calcium, are dissolved to some extent by an aqueous solution of sulphurous acid.

The following table shows the composition of some of the sulphites :—

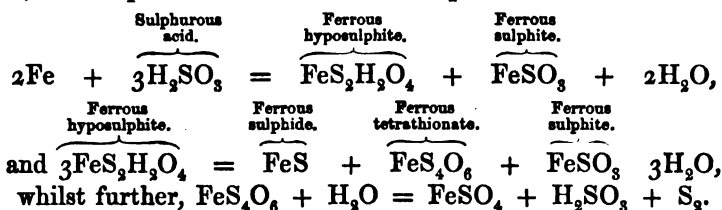
				General formulas.
Sulphurous acid	...	...	...	$\text{H}_2\text{SO}_3$
Normal salt	...	...	...	$\text{M}_2\text{SO}_3$
Acid salt	...	...	...	$\text{HMSO}_3$
Double salt	...	...	...	$\text{MM}'\text{SO}_3$
Potassic sulphite	...	..	...	$\text{K}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$
Hydropotassic sulphite (bisulphite)	...			$\text{KHSO}_3$
Sodic sulphite	...	...	...	$\text{Na}_2\text{SO}_3 \cdot 10\text{H}_2\text{O}$
Hydrosodic sulphite (bisulphite)	...			$\text{NaHSO}_3 \cdot 4\text{H}_2\text{O}$
Calcic sulphite	...	...	...	$\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$
Baric sulphite	...	...	...	$\text{BaSO}_3$
Magnesian sulphite	...	...	...	$\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$
Plumbic sulphite	...	...	...	$\text{PbSO}_3$
Argentiac sulphite	...	...	...	$\text{Ag}_2\text{SO}_3$

Many of the sulphites are decomposed by a strong heat, the acid being gradually expelled. They are also decomposed by sulphuric or by hydrochloric acid, with extrication of sulphurous acid, which is known by its peculiar and pungent odour. The best test for detecting small traces of sulphites consists in the addition of a fragment of zinc and a drop or two of hydrochloric acid to the solution; the sulphurous acid is deoxidized, the sulphur combines with hydrogen, and sulphuretted hydrogen is given off; the gas last named may be detected by suspending a piece of paper moistened with a solution of plumbic acetate, in the upper part of the vessel, which should be closed by a glass plate. Salts of silver in solution give a white precipitate with solutions of the soluble sulphites; the precipitate is soluble in excess of the sulphite, and it is partially reduced to metallic silver when the liquid is boiled: a characteristic reaction is the formation with baric chloride of a white precipitate of baric sulphite, which is soluble in hydrochloric acid, but the solution thus obtained gives a white precipitate of baric sulphate on the addi-



tion of a solution of chlorine, of iodine, or of bleaching powder. The sulphites, when moist, absorb oxygen from the air; and solutions of these salts are often used as deoxidizing agents: for example, the ferric salts are reduced by them to ferrous salts. Gold, selenium, and tellurium, are precipitated by them, from solutions containing excess of hydrochloric acid, in the reduced or metallic form; arsenic acid is reduced to arsenious acid, and chromic acid to a green salt of chromium.

Sulphurous acid dissolves and is decomposed by the metals which, like zinc, iron, tin, and cadmium, evolve hydrogen with hydrochloric acid. Iron, for example, is rapidly dissolved by sulphurous acid if heated with its solution, ferrous sulphite and hyposulphite being formed, whilst the hyposulphite is speedily resolved into ferrous sulphide and tetrathionate; and the tetrathionate in its turn is converted into ferrous sulphate, free sulphur, and sulphurous acid, as is represented in the annexed equations:—



The sulphites are readily formed by transmitting a stream of sulphurous acid through water in which the oxide or the carbonate of the metal is dissolved or suspended, the carbonates being decomposed with effervescence.

(412) **SULPHURIC ACID; Dihydric Sulphate** ( $\text{H}_2\text{SO}_4=98$ ).—This substance, which constitutes one of the most important products of chemical manufacture, is made in enormous quantities. In Great Britain alone upwards of 100,000 tons are annually consumed. The acid is occasionally met with uncombined with bases in thermal springs, particularly in those of volcanic regions. Sulphates of calcium, barium, magnesium, and some other metals, constitute abundant constituents of the crust of the earth.

*Preparation.*—When sulphur is boiled in *aqua regia*, or in concentrated nitric acid, it is gradually oxidized and converted into sulphuric acid; but this method is never employed, excepting for experimental purposes in the laboratory. On the large scale it is made by a process first employed by Roebuck, about the year 1746, since which period the mode of conducting it has undergone several modifications and improvements, though in principle it continues to be the same.

The changes which occur in this process are remarkable and instructive. It has been already mentioned, that when sulphur is burned in air or in oxygen, the product is sulphurous anhydride. This gas, if made to combine with half as much oxygen again as it already contains, is converted into sulphuric anhydride. Direct union, however, cannot be produced between the two gases; the intervention of some third substance becomes necessary; and if water be presented to them, a very gradual combination occurs. If pure and dry oxygen, mixed with twice its bulk of sulphurous anhydride, be transmitted over spongy platinum (65) heated in a tube, the two gases combine, and sulphuric anhydride ( $\text{SO}_2$ ) is produced. Wöhler has also observed, that the two gases unite rapidly when transmitted through a tube heated to incipient redness, and containing a mixture of oxide of copper and sesquioxide of chromium, obtained by precipitation.

The following table represents the composition of sulphuric acid:—

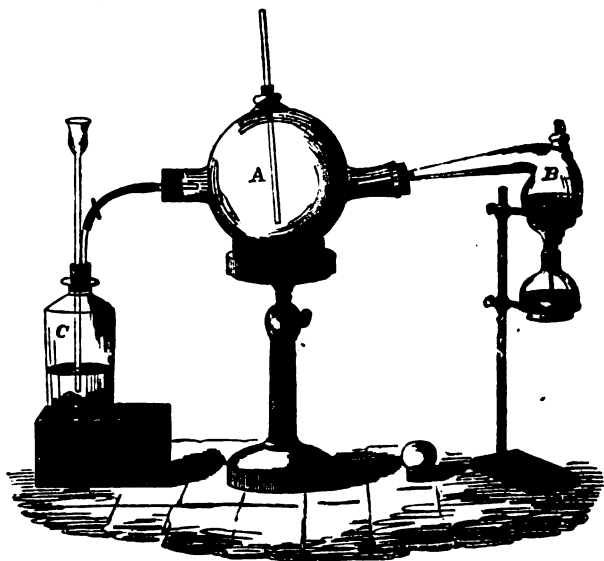
			Anhydride.		Oil of vitriol.	
Sulphur	...	S	= 32	or 40	S	= 32 or 32·65
Oxygen	...	O <sub>2</sub>	= 48	60	O <sub>4</sub>	= 64 65·31
					H <sub>2</sub>	= 2 2·04
			— — —		— — —	
Sulphuric anhydride	}	SO <sub>2</sub>	= 80	or 100	H <sub>2</sub> SO <sub>4</sub>	= 98 100·00

If sulphurous anhydride mixed with oxygen in a moist state be presented to nitric oxide, or to any other of the higher oxides of nitrogen, the combination may be effected with great rapidity; and further, a small proportion of the oxide of nitrogen will suffice to effect the combination of an almost indefinite amount of sulphurous anhydride and oxygen, if water be also present. Upon these facts the process employed in the manufacture of sulphuric acid is founded.

The reaction is easily watched upon the small scale by the following means:—Into a large three-necked receiver, A, fig. 313, filled with atmospheric air, and slightly moistened in the interior, sulphurous anhydride from the retort, B, and nitric oxide from the bottle, C, are made to pass; ruddy fumes of nitric peroxide ( $\text{NO}_2$ ) are immediately formed by the combination of the nitric oxide with atmospheric oxygen, and in a few minutes the inner surface of the receiver becomes coated with a white crystalline deposit, into the composition of which sulphurous anhydride, nitric peroxide, and water enter. As soon as this crystalline mass is treated with water, it is decomposed with brisk effervescence;  $\text{NO}_2 + \text{SO}_2 + x\text{H}_2\text{O}$ , yielding  $\text{NO} + \text{H}_2\text{SO}_4 + x-1\text{H}_2\text{O}$ ; 1 atom of nitric oxide escapes, and 1 atom of sulphuric acid remains in solution: the nitric oxide, by again absorbing oxygen from the air, is reconverted into nitric peroxide; this combines again with a fresh atom of sulphurous anhydride in the presence of a small quantity of water; fresh crystals are formed, and these in their turn are decomposed by solution, as before. The nitric oxide is thus again liberated, and may go through

the same round of compositions and decompositions, till the whole of the oxygen in the air has been consumed: the oxide of nitrogen thus acts the part of a

FIG. 313.



carrier of oxygen to the sulphurous anhydride. In the manufacture of sulphuric acid on the large scale, the formation of the crystalline body and its destruction are simultaneous, if the operation be properly conducted,\* so that no deposition of crystals actually occurs.

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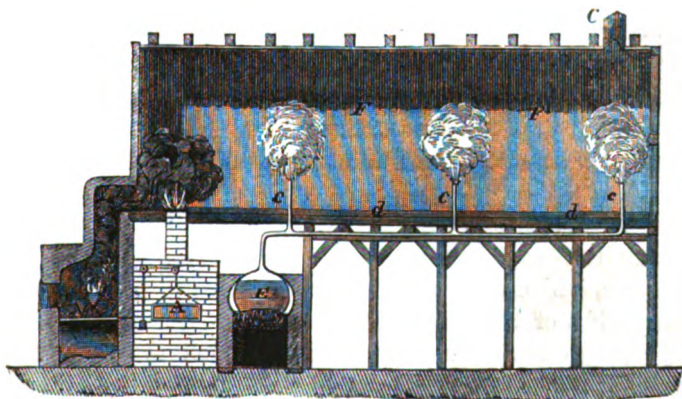
\* The true composition of this crystalline body has been the object of much discussion and numerous experimental inquiries. H. Rose states that by passing pure dry nitric oxide into a glass vessel, from which oxygen is carefully excluded, and the interior of which is moistened with sulphuric anhydride ( $\text{SO}_3$ ), a white, hard, amorphous substance is formed; and this compound he regards as the essential constituent in the crystals above described. It fuses at a high temperature, and may be sublimed without decomposition. Brünig has shown that during the formation of this compound sulphurous anhydride is liberated, in the proportion of 1 atom for every 2 atoms of nitric oxide absorbed; and he found the crystalline compound to have a composition which may be represented by the formula  $(\text{N}_2\text{O}_5, 2\text{SO}_3)$ . Water immediately decomposes it, liberating nitric oxide, whilst sulphuric acid is dissolved. If the anhydrous crystals be exposed to the air, they absorb moisture and emit nitrous fumes. Concentrated sulphuric acid, by the aid of heat, dissolves them in all proportions without change; the solution crystallizes, on cooling, in rectangular prisms, which appear to contain water of crystallization.

Oil of vitriol rapidly absorbs both nitrous anhydride and nitric peroxide, and forms a crystalline compound similar to the foregoing; the addition of water immediately liberates red fumes of nitric peroxide from it.

There are many other methods by which this curious substance may be obtained, but they often involve very complicated considerations. De la Provostaye procures it by the action of liquid sulphurous anhydride on liquid nitric peroxide;

(413) In the manufacture of sulphuric acid, sulphurous anhydride is procured by burning either sulphur, or iron pyrites ( $\text{FeS}_2$ ); provision being made for an abundant supply of atmospheric air to the burning material. The general arrangements adopted in the manufacture are shown in fig. 314. A, A, represent furnaces

FIG. 314.



in which the sulphur is burned: in the current of heated gas an iron pot, *b*, is suspended, which has been previously charged with a mixture of sodic nitrate and oil of vitriol. Vapours of nitric acid are thus liberated; they pass on with the sulphurous anhydride, by suitable flues, into immense chambers, *r, r*, constructed of sheet lead, and supported by a strong timber framework. These chambers are often 12 or 15 feet high, 15 or 20 wide, and from 150 to 300 feet in length, or about 4 or 5 metres high, 5 or 7 broad, and from 50 to 100 metres long; they are sometimes partially intersected by incomplete transverse leaden partitions, interposed in the current of the mixed gases, with a view of effecting their more intimate admixture. Water to the depth of 2 or 3 inches (6 or 8 cm.) is placed upon the floor of the chamber, *d, d*, to condense the acid; and the mutual reaction of the atmospheric oxygen, sulphurous anhydride, and nitric oxide is further facilitated

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he considers it when anhydrous to consist of  $(\text{SO}_3, \text{SO}_3, 2\text{NO}_2)$ , which is consistent with the analysis of Brünig.

Weltzien found that sulphuric acid ( $\text{H}_2\text{SO}_4$ ) combines directly with nitrous anhydride ( $\text{N}_2\text{O}_3$ ), forming a white crystalline mass, in proportions which may be represented by the formula  $(\text{H}_2\text{O}, 2\text{SO}_3, \text{N}_2\text{O}_3)$ . According to the same chemist, sulphuric acid also forms with nitric peroxide a white crystalline compound fusible at  $163^\circ.4$  ( $73^\circ \text{C.}$ ), which, even when the peroxide is present in large excess, contains the two substances in a proportion which may be represented by the formula  $(2\text{H}_2\text{O}, 3\text{SO}_3, 2\text{NO}_3)$ .—*Lieb. Annal.* cxv. 216.

by the injection of steam at a pressure of about 10 lb. upon the inch by means of jets, *c, c, c*, supplied from the boiler, *z*. The nitric acid extricated from the nitre speedily becomes deoxidized by the sulphurous anhydride to the state of nitric oxide ( $3\text{SO}_2 + 2\text{HNO}_3 + 2\text{H}_2\text{O} = 2\text{NO} + 3\text{H}_2\text{SO}_4$ ), and then the changes already pointed out succeed each other rapidly, and sulphuric acid is formed in large quantity.

In a properly managed chamber, the gases which pass off by the exit flue, *c*, consist only of nitrogen and nitric oxide, the sulphurous anhydride and oxygen being supplied in quantities just sufficient to effect their mutual condensation, fresh atmospheric air entering at the other end along with the sulphurous anhydride.

Gay-Lussac has taken advantage of the solubility of nitric oxide in oil of vitriol, to economize the consumption of nitre in the process, which upon the old plan amounts to from one-eighth to one-twelfth of the weight of the sulphur consumed. By the contrivance to be mentioned immediately, the quantity of nitre formerly requisite has been reduced by one-half, or even by two-thirds. The improvement consists in conducting the spent gases into a leaden tower filled with fragments of coke, through which a stream of concentrated sulphuric acid is continually trickling. The acid thus becomes charged with the nitrous vapours, and flows off at the bottom of the tower to a reservoir from which it is again raised by a forcing-pump to the top of a second similar tower at the entrance of the chamber, where it is deprived of the nitrous compounds by the sulphurous anhydride as it enters from the furnace.

The sulphuric acid which collects at the bottom of the chambers is in too dilute a condition for sale: it is not found advantageous to allow it to attain a degree of concentration greater than 1·60 in the chambers, since beyond this it becomes liable to absorb and retain the nitrous fumes.\* When it has reached a specific gravity of about 1·60, it is sufficiently strong for the manufacture of salt-cake, but it requires concentration for other purposes: with this view it is drawn off and evaporated in shallow leaden pans till it has acquired a density of 1·720; beyond this point the concentration cannot be carried in these vessels, because the temperature required would endanger the melting of the leaden pan and its corrosion by the acid. This acid of sp. gr. 1·720 forms

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\* The crude acid of sp. gr. 1·60 does not usually contain more than 0·6 per cent. of nitrous acid (Mr. Allhusen).

the *brown acid* of commerce; it is extensively employed in the manufacture of the so-called superphosphate of lime for manures, and for other coarse purposes. When required in a still more concentrated form, the brown acid is transferred into glass retorts, or, as is practised in many works, into platinum stills; the presence of nitrous compounds must be avoided when platinum is employed, otherwise the metal is gradually corroded; in these it is again further heated until white fumes of oil of vitriol pass over. Beyond this point it is useless to carry the operation, as the concentrated acid distils over. Indeed, during the whole operation some acid passes over with the water, which is therefore preserved, and returned to the leaden chamber.

The acid that remains in the retort after it has thus been boiled down, is the concentrated *oil of vitriol* of commerce; it is a definite compound, consisting of  $\text{H}_2\text{SO}_4$ . De Marignac (*Ann. de Chimie*, III. xxxix. 189) finds that it always contains a slight excess of water beyond the atomic proportion calculated from the formula  $\text{H}_2\text{O}, \text{SO}_3$ : instead of 18·36 per cent. of water, he always obtained 19·62; and a similar observation was made by Gay-Lussac. Playfair states that, if the concentration of the acid be effected by a temperature not exceeding  $500^\circ$  ( $260^\circ \text{C.}$ ), the true compound  $\text{H}_2\text{SO}_4$  of sp. gr. 1·848 is obtained; but if heated to ebullition, it is partially decomposed in the manner stated by De Marignac.

*Strength of Sulphuric Acid of Different Densities at  $60^\circ$   
( $15^\circ\cdot5 \text{C.}$ ) (Ure).*

Specific gravity.	$\text{SO}_3$ in 100 pts.	$\text{H}_2\text{SO}_4$ .	Specific gravity.	$\text{SO}_3$ in 100 pts.	$\text{H}_2\text{SO}_4$ .	Specific gravity.	$\text{SO}_3$ in 100 pts.	$\text{H}_2\text{SO}_4$ .
1·8460	81·54	100	1·5503	53·82	66	1·2334	26·09	32
1·8415	79·90	98	1·5280	52·18	64	1·2184	24·46	30
1·8366	78·28	96	1·5066	50·55	62	1·2032	22·83	28
1·8288	76·65	94	1·4860	48·92	60	1·1876	21·20	26
1·8181	75·02	92	1·4660	47·29	58	1·1706	19·57	24
1·8070	73·39	90	1·4460	45·66	56	1·1549	17·94	22
1·7901	71·75	88	1·4265	44·03	54	1·1410	16·31	20
1·7728	70·12	86	1·4073	42·40	52	1·1246	14·68	18
1·7540	68·49	84	1·3884	40·77	50	1·1090	13·05	16
1·7315	66·86	82	1·3697	39·14	48	1·0953	11·41	14
1·7080	65·23	80	1·3530	37·51	46	1·0809	9·78	12
1·6860	63·60	78	1·3345	35·88	44	1·0682	8·15	10
1·6624	61·97	76	1·3165	34·25	42	1·0544	6·52	8
1·6415	60·34	74	1·2999	32·61	40	1·0405	4·89	6
1·6204	58·71	72	1·2826	30·98	38	1·0268	3·26	4
1·5975	57·08	70	1·2654	29·35	36	1·0140	1·63	2
1·5760	55·45	68	1·2490	27·72	34	1·0074	0·815	1

The preceding table gives the proportion of sulphuric acid contained in solutions of the densities therein mentioned.\*

(414)  $\text{H}_2\text{SO}_4$ , sometimes called *Protohydrate of Sulphuric Acid*.—The oil of vitriol of commerce forms a dense, oily-looking, colourless liquid, without smell, and of specific gravity 1·842. It is intensely caustic, and chars almost all organic substances, from its powerful attraction for moisture. With water it mixes completely in all proportions, and the mixture, when cold, occupies less bulk than the two liquids did when separate. Great heat is given out at the moment the mixture is made; the dilution should therefore be performed gradually, always pouring the acid into the water, not the water into the acid. So powerful is the attraction of the acid for moisture, that if it be exposed in a shallow dish to the air for a few days, it frequently doubles its weight by absorbing aqueous vapour from the air. In the laboratory, advantage is very often taken of this property, which enables it to be employed in a variety of cases as a desiccating agent (66 and 185). The acid of commerce is sometimes of a dark brown colour, occasioned by its charring action on fragments of organic matter, such as straw or wood, which have accidentally fallen into it. Sulphuric acid does not evaporate at the ordinary temperature of the air. If a drop of the diluted acid fall upon a cloth, the water gradually evaporates until the acid which is left behind acquires a certain degree of concentration. On approaching a fire or other source of heat, a further portion of the water is expelled, and the acid becomes more concentrated, until it chars or destroys the cohesion of the fibres; this is one cause of the destructive action of sulphuric acid upon linen, even when very much diluted.

De Marignac finds that the true sulphuric acid ( $\text{H}_2\text{SO}_4$ ) when heated emits a small quantity of the vapour of the anhydride, and the remaining liquid boils at  $640^{\circ}\cdot 4$  ( $338^{\circ}\text{C}.$ ). Bineau states that just above the boiling-point of the acid the vapour has a sp. gr. of 2·15,

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\* Bineau has more recently made a careful determination of the strength of sulphuric acid of different densities (*Ann. de Chimie*, III. xxiv. 341), but his results differ but slightly from those of Ure, as may be seen from the annexed table, temp.  $59^{\circ}$  ( $15^{\circ}\text{C}.$ ):—

Specific gravity.	$\text{H}_2\text{SO}_4$ in 100 parts.	Specific gravity.	$\text{H}_2\text{SO}_4$ in 100 parts.	Specific gravity.	$\text{H}_2\text{SO}_4$ in 100 parts.
1·842	100	1·501	60	1·144	20
1·822	90	1·398	50	1·068	10
1·734	80	1·306	40	1·032	5
1·615	70	1·223	30		

which would represent 2 volumes of the anhydride and 2 volumes of steam (1 atom of each) condensed into the space of 3 volumes, but it continues to expand by heat until at  $878^{\circ}$  ( $470^{\circ}$  C.) an atom of the compound occupies the space of 4 volumes, which would reduce the density of the vapour to 1.692. This by some chemists is supposed to be produced by the separation of the compound into aqueous vapour and anhydride by the process of dissociation (see *note*, Part I. p. 103). After the acid has been frozen, it melts at  $51^{\circ}$  ( $10^{\circ}.5$  C.), but it may be cooled much below this point without solidifying. On dropping into the cooled acid a crystal of the acid previously frozen, congelation immediately occurs, and the temperature rises to  $51^{\circ}$ . The concentrated acid of commerce does not usually freeze till it has been cooled to about  $-29^{\circ}$  ( $-34^{\circ}$  C.); but when frozen it does not become liquid till the temperature reaches  $32^{\circ}$  ( $0^{\circ}$  C.).

( $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ ) or *Second Hydrate of Sulphuric Acid*.—If water be added to sulphuric acid, until the density is reduced to 1.78, a definite hydrate is formed. It freezes at  $47^{\circ}$  ( $8^{\circ}.3$  C.), and crystallizes in splendid rhombic prisms, the sp. gr. of which is 1.951; from this property it is often termed *glacial sulphuric acid*. According to Dalton, it boils at  $435^{\circ}$  ( $224^{\circ}$  C.). Graham found that this hydrate may be obtained by heating a more diluted acid to  $400^{\circ}$  ( $204^{\circ}.5$  C.) till it ceases to give off water.

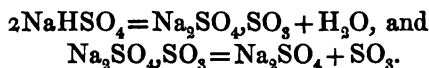
Another *hydrate* ( $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ ) may, according to Graham, be procured by evaporating a dilute acid *in vacuo* at  $100^{\circ}$  C., till it ceases to lose weight. The density of this hydrate is 1.632, and its boiling-point is  $348^{\circ}$  ( $175^{\circ}.5$  C.).

(415) *Nordhausen Sulphuric Acid*.—For the purpose of dissolving indigo in the process of dyeing Saxony blue, an acid of still higher concentration than oil of vitriol is required. Such an acid is principally prepared at the town of Nordhausen, in Saxony, and is hence known as *Nordhausen oil of vitriol*. The old name for ferrous sulphate was *green vitriol*, and this circumstance, taken in conjunction with the oily consistence of the concentrated acid, gave rise to the name of *oil of vitriol*, by which the concentrated acid of commerce is still frequently known, and which is convenient as distinguishing it from more diluted acids. In preparing the Nordhausen acid, ferrous sulphate is dried at a moderate heat to expel its water of crystallization, and is then distilled in earthen retorts; a dense, brown, fuming liquid passes over, of sp. gr. about 1.9.

(416) *Sulphuric Anhydride* ( $\text{SO}_3=80$ ); *Rel. wt.* 40; *Mol. Vol.*   .—If this fuming Nordhausen acid be placed in a glass retort, furnished with a receiver which is kept cool by ice, and a gentle heat be applied to the retort, white fumes pass over, which solidify into a white, silky-looking fibrous mass. This is the compound formerly called *anhydrous sulphuric acid*. The remainder



in the retort, after all the anhydride is expelled, consists of ordinary oil of vitriol. Sulphuric anhydride may also be obtained from the hydro-sodic sulphate ( $\text{NaHSO}_4$ ), which melts at a dull red heat, and is deprived of its hydrogen in the form of water; after which, if distilled in an earthen retort, it yields white fumes of the anhydride, whilst disodic sulphate remains in the retort:—



The anhydride forms with oil of vitriol a compound ( $\text{H}_2\text{SO}_4 \cdot \text{SO}_3$ ) that crystallizes in plates which fuse at  $95^\circ$  ( $35^\circ$  C.).

Sulphuric anhydride, however, possesses no acid properties. It is tough, ductile, and can be moulded in the fingers, like wax, without charring the skin. It fumes in the air, and is very deliquescent: when thrown into water the heat emitted is so intense that it hisses as a hot iron would do. The solution has all the properties of ordinary sulphuric acid. The anhydride melts at  $65^\circ$  ( $18^\circ\cdot3$  C.), and boils at about  $110^\circ$  ( $43^\circ\cdot3$  C.), forming a colourless vapour, which, if passed through ignited porcelain tubes, is decomposed into 2 volumes of sulphurous anhydride and 1 of oxygen; 1 volume of sulphur vapour and 3 of oxygen being condensed in the anhydride into the space of 2 volumes of vapour. The specific gravity of this vapour was found by Mitscherlich to be  $3\cdot01$ , or somewhat higher than its calculated amount, which is  $2\cdot764$ : for

			By weight.		By volume.		Sp. gr.
Sulphur ...	S =	32	or 40	1	or 0·5	=	1·1056
Oxygen ...	O <sub>3</sub> =	48	60	3	1·5	=	1·6584
<hr/>							
Sulphuric anhydride } SO <sub>3</sub> =	80		100	2	1	=	2·7640

According to De Marignac, sulphuric anhydride exists under two modifications one of which melts at about  $65^\circ$  ( $18^\circ\cdot3$  C.), and is produced by distillation, or by fusion at a high temperature; but when once it has been solidified, it passes rapidly into the other form, which melts near  $212^\circ$ , at which temperature it is slowly volatilized, and becomes reconverted into the first variety. Sulphuric anhydride in some cases combines with the anhydrous bases; if its vapour be passed over baryta heated to the point of redness, the two combine with incandescence, and baric sulphate is formed. Mercury when heated in the vapour, is converted into mercuric sulphate with liberation of sulphurous anhydride. Phosphorus takes fire in its vapour, setting sulphur free.

Sulphuric anhydride combines with sulphur, forming solutions which have a brown, green, or blue colour, according to the proportion of sulphur; the blue compound containing the smallest proportion. It likewise dissolves iodine, and with one-tenth of its weight of iodine forms a green crystalline compound. It also combines with hydrochloric acid, and forms a liquid termed *chlorhydrosulphuric acid* ( $\text{HCl} \cdot \text{SO}_3$ ), which boils at  $293^\circ$  ( $145^\circ$  C.), and is decomposed by

water. Williamson obtained it by the action of phosphoric chloride upon sulphuric acid;  $\text{H}_2\text{SO}_4 + \text{PCl}_5 = \text{HCl}_2\text{SO}_4 + \text{HCl} + \text{POCl}_3$ ; hydrochloric acid and phosphoric oxytrichloride being formed at the same time.

We are therefore acquainted with the following definite compounds of sulphuric anhydride with water; starting with the anhydride:—

Hydrate.	Formula.	Fusing point.		Boiling point.		Specific gravity.
		° C.	° F.	° C.	° F.	
Sulphuric anhydride ...	$\text{SO}_3$	18.3	65			
Anhydro-sulphuric acid	$\text{H}_2\text{SO}_4, \text{SO}_3$	25	95			
Oil of vitriol ...	$\text{H}_2\text{SO}_4$	10.5	51	338	640	1.848
Glacial acid ...	$\text{H}_2\text{SO}_4, \text{H}_2\text{O}$	8.3	47	224	435	1.780
Graham's hydrate ...	$\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$			176	348	1.632

*Uses.*—The applications of sulphuric acid in the arts are very numerous. Immense quantities of it are consumed in the manufacture of sodic sulphate as a preliminary process in making sodic carbonate; and it is in constant requisition for the preparation of nitric, hydrochloric, and other volatile acids. Its applications in the laboratory are too numerous to be specified.

(417) *Impurities common in the Commercial Acid.*—The oil of vitriol of commerce is never pure: it always contains lead, derived from the vessels in which it is made. The greater part of the plumbic sulphate is precipitated as a white powder when the acid is diluted. It is also frequently contaminated with arsenious acid, derived from the pyrites: the diluted acid in this case gives a yellow precipitate when exposed to a current of sulphuretted hydrogen gas. The arsenic is still more easily recognized by what is termed Marsh's test, which will be described under the head of arsenic (846). On the large scale this impurity is effectually removed by adding a small quantity of baric sulphide to the acid; orpiment ( $\text{As}_2\text{S}_3$ ) and baric sulphate are formed; they are both insoluble in the acid, and may be separated by subsidence and decantation. The greater part of the arsenious acid may also be got rid of by adding hydrochloric acid and boiling the liquid, when the arsenic is expelled in the form of arsenious chloride with the excess of hydrochloric acid. Nitric acid and some of the lower oxides of nitrogen are also often present: a strong solution of green vitriol in water, when added to the undiluted acid, shows the presence of these impurities by striking a characteristic purplish-red colour at the point of contact of the two liquids. Sulphurous acid may likewise sometimes be detected in the acid, as may also hydrochloric acid and potassic sulphate.

When required in a pure form, the acid must be re-distilled

with a little ammoniac sulphate; this salt decomposes any nitrous acid which may be present (p. 112). The distillation requires to be conducted with much care, as the boiling takes place with violent concussions and sudden bursts of vapour: the danger may be avoided by distilling it from freshly broken crystals of quartz; or by using a gas-burner in the form of a large ring, so as to apply heat to the sides only of the retort, in which case the insoluble matters collect at the bottom, whilst the ebullition takes place tranquilly from the sides.

(418) Sulphuric acid in its concentrated form acts but feebly upon metallic bodies in the cold, but when boiled upon them it in some cases undergoes decomposition: even silver is dissolved by it, sulphurous anhydride being formed, whilst the sulphate of the metal is dissolved in the excess of sulphuric acid; for example,  $\text{Ag}_3 + 2\text{H}_2\text{SO}_4 = \text{Ag}_2\text{SO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$ . Copper, mercury, arsenicum, antimony, bismuth, tin, lead, and tellurium are acted upon by the acid in a similar manner. Gold, platinum, rhodium, and iridium are not acted upon by sulphuric acid even when boiled with it. The more oxidizable metals are dissolved by this acid when diluted with water, hydrogen being liberated, whilst the metal unites with sulphion ( $\text{SO}_4$ ), forming a sulphate: zinc, iron, cobalt, nickel, and manganese are acted upon in this way. The acid is also decomposed when boiled with charcoal or with sulphur, sulphurous anhydride being evolved.

*Sulphates.*—Sulphuric acid is at common temperatures the most energetic of the acids, displacing from their salts all acids which boil at a lower temperature than itself. The salts formed by this acid are termed *sulphates*. With the alkalis it forms acid salts, such as acid sulphate of potassium, or hydro-potassic sulphate ( $\text{KHSO}_4$ ): in a few instances basic salts, such as the basic sulphate of copper ( $\text{CuSO}_4 \cdot 2\text{CuH}_2\text{O}_2$ ), may be formed. Many of the sulphates occur native, and constitute important and well-known minerals, such, for instance, as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and the sulphates of barium, strontium, and lead. Some are formed by the spontaneous or artificial oxidation of the sulphides, as, for instance, the sulphides of iron and copper, which, by exposure to the weather, or by roasting, can furnish the sulphates of the metals. The soluble sulphates of the metals may be readily prepared by dissolving in diluted sulphuric acid either the metal itself, or its oxide or carbonate in cases in which the metal is not readily attacked by the acid. The insoluble sulphates, such as those of barium and lead, may be obtained by precipitating a soluble salt of the metal by means of some soluble sulphate, such

as sodic sulphate. Many of the sulphates are formed as residues during the preparation of the volatile acids by the action of sulphuric acid on their salts. Potassic sulphate is thus obtained during the preparation of nitric acid from saltpetre, sodic sulphate as a residue from common salt in the manufacture of hydrochloric acid, and so on. The sulphates of potassium, barium, strontium, lead, silver, and both mercurous and mercuric sulphate, are anhydrous. Calcic sulphate (gypsum) contains  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The sulphates of zinc, magnesium, iron, cobalt, and nickel, usually crystallize with  $7\text{H}_2\text{O}$ ; but the number of atoms of water in these salts is often smaller if the solution be allowed to crystallize at a high temperature, the proportion of water being sometimes 5, at others 4, and under some circumstances as low as  $2\text{H}_2\text{O}$ . The sulphates of the group isomorphous with magnesian sulphate contain 1 atom of water which admits of displacement by an atom of some anhydrous sulphate, such as potassic sulphate or ammoniac sulphate: peculiar double salts are thus formed, which retain 6 atoms of water of crystallization, but these double salts are still isomorphous with magnesian sulphate (555). Cupric sulphate crystallizes with  $5\text{H}_2\text{O}$ , but it forms double salts containing  $6\text{H}_2\text{O}$ : such as  $(\text{CuSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O})$  isomorphous with those just mentioned. Sodic sulphate crystallizes usually as  $(\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O})$ , but it exhibits some singular anomalies (586).

Neither plumbic sulphate nor the sulphates of the metals of the alkalis and alkaline earths are decomposed when heated to redness, except magnesian sulphate, which loses its acid partially; the sulphates of zinc, cadmium, nickel, cobalt, copper, and silver require an intense heat to decompose them; but the other sulphates part with their acid without difficulty when strongly ignited. When heated with charcoal the sulphates are all decomposed; those of the metals of the alkalis and alkaline earths being converted into sulphides: these sulphides, when moistened with hydrochloric acid, evolve sulphuretted hydrogen. Baric sulphate may be easily recognized, even in small quantity, if, after having been mixed with a little charcoal and folded in a piece of platinum foil, it is heated in the flame of the blowpipe;  $\text{BaSO}_4 + 4\text{C} = \text{BaS} + 4\text{CO}$ ; the carbonic oxide escaping as gas; the baric sulphide, when moistened with hydrochloric acid, is converted into baric chloride, and evolves hydrosulphuric acid;  $\text{BaS} + 2\text{HCl} = \text{BaCl}_2 + \text{H}_2\text{S}$ . The sulphates of the metals of the alkalis and alkaline earths may also be converted into sulphides by heating them to redness in a glass or porcelain tube, and transmitting a current of dry hydrogen gas over them. In this

way potassic sulphate is reduced without difficulty to sulphide, water being formed;  $K_2SO_4 + 4H_2 = K_2S + 4H_2O$ .

Sulphuric acid is dibasic. The composition of some of the more important sulphates is shown in the following list:—

				General formulæ.
Neutral salt	...	...	...	$M_2SO_4$
Acid salt	...	...	...	$MHSO_4$
Double salt	...	...	...	$M'MSO_4$
<hr/>				
Potassic sulphate	...	...	...	$K_2SO_4$
Sodic	"	...	...	$Na_2SO_4, 10H_2O$
Hydro-potassic sulphate (bisulphate)				$KHSO_4$
Ammonic sulphate	...	...	...	$(H_4N)_2SO_4$
Calcic	"	...	...	$CaSO_4, 2H_2O$
Baric	"	...	...	$BaSO_4$
Strontic	"	...	...	$SrSO_4$
Plumbic	"	...	...	$PbSO_4$
Argentie	"	...	...	$Ag_2SO_4$
Magnesian	"	...	...	$MgSO_4, 7H_2O$
Zincic	"	...	...	$ZnSO_4, 7H_2O$
Ferrous	"	...	...	$FeSO_4, 7H_2O$
Cobalt	"	...	...	$CoSO_4, 7H_2O$
Cupric	"	...	...	$CuSO_4, 5H_2O$
Aluminic	"	...	...	$Al_2(SO_4)_3, 18H_2O$
Potash-alum	...	...	...	$KAl_2(SO_4)_3, 12H_2O$
Cuprico-dipotassic sulphate	...	...	...	$CuSO_4, K_2SO_4, 6H_2O$
Basic sulphate of copper	...	...	...	$CuSO_4, 2CuH_2O_2$

**Tests.**—Sulphuric acid and its salts are easily recognized when in solution by the white precipitate of baric sulphate which is formed on the addition of baric nitrate; this precipitate is very insoluble in nitric acid. A white precipitate of plumbic sulphate, nearly as insoluble as baric sulphate, is formed on adding a soluble salt of lead to a solution containing sulphuric acid or a sulphate. The sulphates of strontium, calcium, and silver are but sparingly soluble in water; the others are readily soluble; nearly all the sulphates are insoluble in alcohol, unless a large excess of acid be present. The sulphates which are insoluble in water and in acids may be entirely decomposed by fusion with an excess of sodic or potassic carbonate, a sulphate of the alkali-metal being formed, which may be dissolved by water, whilst an insoluble carbonate of the other metal is left. A solution of either potassic or sodic carbonate, when boiled with the insoluble sulphates, produces a similar but less complete decomposition.

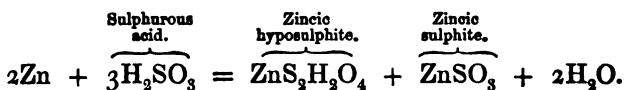
(419) **HYPOSULPHUROUS ACID**;  $H_2S_2H_2O_4 = 132$ .—Of the remaining acids of sulphur, the only one of any practical importance is the hyposulphurous or *dithionous* acid. Its sodium salt has been

largely employed in the fixing of photographic pictures. This application has arisen from the power possessed by this compound of dissolving those argentic haloid salts which are insoluble in water, forming with them soluble double salts; the surface of the photograph is freed from the unaltered argentic compound by immersion in a solution of the hyposulphite, whilst the portion which has been blackened by light is left unacted upon; if, after this operation, the picture be well washed with water, it is no longer liable to alteration by exposure to light.

Besides its application in photography, the sodic hyposulphite is employed to a considerable extent as an *antichlore*, for removing the last traces of chlorine from the bleached pulp employed in paper-making; and it has been proposed by Percy as a solvent in the separation of argentic chloride for metallurgical purposes.

Rose states that none of the hyposulphites can be obtained in the anhydrous form, all of them retaining at least 1 atom of water which cannot be expelled without completely decomposing the salt, so that their true formula should be  $M'S_2H_2O_4$ ; that of the barium salt, for instance, instead of being  $Ba''S_2O_3 \cdot H_2O$ , should be  $Ba''S_2H_2O_4$ .

If zinc filings be digested in a solution of sulphurous acid, the metal is dissolved without any extrication of gas; it is oxidized at the expense of a portion of the sulphurous acid, and a mixture of zincic sulphite and hyposulphite is found in solution:—



*Sodic hyposulphite* (*hyposulphite of soda*;  $Na_2S_2H_2O_4 \cdot 4H_2O$ ; *Sp. Gr.* 1.672), is manufactured to some extent from impure sulphide of sodium (prepared by fusing together in a covered crucible equal weights of sodic carbonate and powdered sulphur, or by converting sodic sulphate into sulphide, by calcining the sulphate with carbon), by transmitting through a solution of it, a stream of gaseous sulphurous anhydride until it ceases to be absorbed; the liquid is then filtered and evaporated; sodic hyposulphite crystallizes in bold striated rhombic prisms, terminated by oblique faces. A still better plan consists in digesting a solution of sodic sulphite on powdered sulphur; the sulphur is gradually dissolved and forms a colourless solution, which on evaporation yields crystals of sodic hyposulphite, 1 atom of sulphur and 1 of water combining with 1 atom of sodic sulphite;  $Na_2SO_3 + H_2O + S$  becoming  $Na_2S_2H_2O_4$ . When heated in closed vessels the hyposulphite first loses water, and is then resolved into

sodic sulphate and pentasulphide ;  $4\text{Na}_2\text{S}_3\text{H}_2\text{O}_4 = 4\text{H}_2\text{O} + 3\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_5$ .

The *hyposulphites of calcium and strontium* ( $\text{CaS}_2\text{H}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{SrS}_2\text{H}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ ), may be prepared by transmitting sulphurous acid through the sulphides of calcium and strontium suspended in water ; their solutions are decomposed below the temperature of  $212^\circ$  into free sulphur and sulphites of the earths.

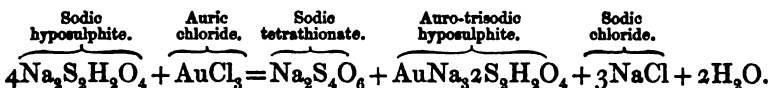
Calcic hyposulphite is formed spontaneously in large quantity in the refuse lime from the gas-works, and in the refuse from the ball soda of the alkali works ; they consist chiefly of a mixture of calcic sulphide with lime and calcic carbonate, and are now employed as valuable sources of sodic hyposulphite, which is readily obtained from them by double decomposition with sodic carbonate.

*Baric hyposulphite* ( $\text{BaS}_2\text{H}_2\text{O}_4$ ) may be obtained in small brilliant crystals by mixing dilute solutions of baric chloride and sodic hyposulphite. It is impossible, however, to obtain the acid in the form of a hydrate either from this or from any of its salts ; when, for example, sulphuric acid is added to baric hyposulphite, baric sulphate is precipitated ; but if the solution be filtered, the clear liquid speedily becomes milky from the separation of sulphur, and the odour of sulphurous anhydride is emitted ;  $\text{H}_2\text{S}_2\text{H}_2\text{O}_4$  becoming decomposed into  $\text{S} + \text{SO}_2 + 2\text{H}_2\text{O}$ .

The soluble hyposulphites are easily recognized by the facility with which they dissolve argentic chloride, forming the argento-sodic hyposulphite, which yields a solution of an intensely sweet taste ;  $\text{AgCl} + \text{Na}_2\text{S}_2\text{H}_2\text{O}_4 = \text{NaCl} + \text{NaAgS}_2\text{H}_2\text{O}_4$ . Solutions of the hyposulphites give a white precipitate of plumbic hyposulphite in solutions of the salts of lead ; this precipitate, however, becomes decomposed and blackened if dried at  $212^\circ$ , owing to its partial conversion into plumbic sulphide ; a solution of mercurous nitrate is immediately decomposed by a solution of the hyposulphites at ordinary temperatures in a similar manner, the black sulphide of mercury being deposited. These salts also give a brown precipitate, consisting of cupric sulphide, when heated with a solution of a cupric salt acidulated with hydrochloric acid. An alcoholic solution of iodine is rendered colourless by admixture with an excess of hyposulphite, a tetrathionate of the metal being produced (422).

*Auro-trisodic hyposulphite*, or *Hyposulphite of gold and sodium* ( $\text{AuNa}_3\text{S}_2\text{H}_2\text{O}_4$ ) is used for gilding the daguerreotype plate, and for colouring the positive proof obtained in photographic printing. It may be prepared in a state of purity by mixing concentrated solutions of 1 part of auric chloride and 3

parts of sodic hyposulphite : sodic chloride, sodic tetrathionate, and hyposulphite of sodium and gold being formed : on the addition of alcohol the latter salt is precipitated ; the precipitate must be redissolved in a small quantity of water, and again precipitated by alcohol. It crystallizes in groups of colourless needles, which are very soluble in water, but insoluble in alcohol. It may be mixed with diluted sulphuric or hydrochloric acid without the evolution of sulphurous acid. The formation of this double salt is explained by the following equation (Fordos and Gélis, *Ann. de Chimie*, III. xiii. 399) :—



(420) HYPOSULPHURIC ACID: *Dithionic acid*; *Dihydric dithionate*;  $\text{H}_2\text{S}_2\text{O}_6 = 162$ .—This acid is more stable than the hyposulphurous acid, and may be obtained in solution in water. If sulphurous anhydride be transmitted through water in which finely divided peroxide of manganese is suspended, the gas is rapidly absorbed, and if the liquid be kept cool, manganous hyposulphate is formed;  $\text{MnO}_2 + 2\text{SO}_2$ , yielding  $\text{MnS}_2\text{O}_6$ . If the temperature be allowed to rise, manganous sulphate is formed instead;  $\text{MnO}_2 + \text{SO}_2$ , becoming  $\text{MnSO}_4$ . It is difficult to prevent the formation of a little of the latter salt, but the two salts are easily separated; by adding baryta-water manganese is precipitated as hydrated protoxide, and baric sulphate and hyposulphate are formed;  $\text{MnSO}_4 + \text{MnS}_2\text{O}_6 + 2\text{BaH}_2\text{O}_4 = \text{BaSO}_4 + \text{BaS}_2\text{O}_6 + 2\text{MnH}_2\text{O}_4$ . The baric hyposulphate, being soluble, may be separated from the insoluble baric sulphate by filtration, and it may be obtained in prismatic efflorescent crystals ( $\text{BaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ ) by evaporation below  $41^\circ$  ( $5^\circ \text{C}$ .): at higher temperatures it yields permanent crystals, with only 2 atoms of water, which belong to the oblique system. By the cautious addition of diluted sulphuric acid to its solution, until a precipitate ceases to be formed on the addition of a drop of sulphuric acid, hyposulphuric acid is liberated, and may be filtered from the baric sulphate.

Many double hyposulphates may be obtained, such as the bario-disodic hyposulphate ( $\text{BaNa}_2\text{S}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ ), and the corresponding silver salt ( $\text{AgNaS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ ).

The hyposulphates are all soluble in water. The solid salts when heated emit sulphurous anhydride, whilst a sulphate of the metal remains behind. When in solution they may be oxidized at a boiling heat by chlorine or by nitric acid, and two atoms of sulphuric acid are formed;  $2\text{H}_2\text{S}_2\text{O}_6 + 2\text{H}_2\text{O} + \text{O}_2 = 4\text{H}_2\text{SO}_4$ . In the cold, they present no appearance of decomposition when treated with sulphuric acid, but if heated with it, sulphurous anhydride is evolved, but no deposit of sulphur occurs. These reactions distinguish the hyposulphates from both the sulphites and hyposulphites.

(421) TRITHIONIC ACID; *Dihydric trithionate*; ( $\text{H}_2\text{S}_3\text{O}_6 = 194$ ).—If a saturated solution of hydro-potassic sulphite ( $\text{KHSO}_3$ ) be digested on powdered sulphur for three or four days, till the yellow colour which the liquid acquires at first has disappeared, sulphurous anhydride gradually escapes and potassic trithionate ( $\text{K}_2\text{S}_3\text{O}_6$ ) is formed. It crystallizes in anhydrous four-sided prisms, terminated by dihedral summits. A solution of the salt gives a black precipitate with mercurous nitrate, and a white with the mercuric nitrate; with argentic nitrate it gives a yellowish-white precipitate, which soon becomes black. Potassic trithio-



nate may be decomposed by means of tartaric acid, and the liberated trithionic acid has even been obtained in prismatic crystals, but its solution gradually undergoes spontaneous decomposition into sulphur and sulphurous and sulphuric acids;  $\text{H}_2\text{O} + \text{H}_2\text{S}_3\text{O}_6 = \text{S} + \text{H}_2\text{SO}_3 + \text{H}_2\text{SO}_4$ . When the trithionates are heated in a closed tube, sulphur is sublimed, sulphurous anhydride is expelled, and sulphate of the metal is left.

(422) TETRATHIONIC ACID; *Dihydric tetrathionate*; ( $\text{H}_2\text{S}_4\text{O}_6 = 226$ ).—When baric hyposulphite is suspended in water, and iodine is added, baric iodide is formed, and a new, sparingly soluble salt, baric tetrathionate, is separated in hydrated crystals which contain 2 atoms of water:  $2\text{BaS}_2\text{O}_4 + \text{I}_2 = \text{BaI}_2 + \text{BaS}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ . The tetrathionate is purified by recrystallization; and from a solution of this salt a pure solution of tetrathionic acid may be prepared by the addition of a quantity of sulphuric acid just sufficient to precipitate the whole of the barium; the acid may be concentrated *in vacuo* over sulphuric acid. By boiling the solution, sulphur is deposited, sulphurous anhydride escapes, and sulphuric acid remains in the liquid.

(423) PENTATHIONIC ACID:  $\text{H}_2\text{S}_5\text{O}_6 = 258$ .—A solution of sulphurous acid is decomposed by transmitting through it a current of sulphuretted hydrogen; sulphur is deposited, and a new acid remains in the liquid;  $10\text{H}_2\text{SO}_3 + 10\text{H}_2\text{S} = 2\text{H}_2\text{S}_5\text{O}_6 + 5\text{S}_2 + 18\text{H}_2\text{O}$ . It is very unstable: tetrathionic and trithionic acids are formed by the decomposition of its solution, attended with a deposition of sulphur. *Baric pentathionate* ( $\text{BaS}_5\text{O}_6 \cdot 2\text{H}_2\text{O}$ ) may be obtained in silky scales by neutralizing the acid with baryta-water, and precipitating the salt from its aqueous solution by the addition of alcohol: mercurous nitrate gives a yellow precipitate in its solution; and argentic nitrate a yellow precipitate, which quickly becomes decomposed and turns black.

*Tests for the Acids of Sulphur.*—The action of sulphuric acid upon the salts of the various oxy-acids of sulphur, affords a simple means of distinguishing between several of these different classes of salts. When concentrated sulphuric acid is poured upon the sulphates, it evolves no odour, even when heated with them. The sulphites, even in the cold, yield, with diluted sulphuric acid, an odour of sulphurous acid. The hyposulphates emit no odour of sulphurous acid with diluted sulphuric acid in the cold, but evolve sulphurous acid by the aid of heat: whilst diluted sulphuric acid produces with the hyposulphites, even in the cold, an odour of sulphurous acid attended with a deposit of sulphur.

(424) *Sulphuryl Chloride*, or *Chlorosulphuric Acid* ( $\text{SO}_2\text{Cl}_2 = 135$ ; *Sp. Gr. of Liquid*, 1.66; *of Vapour, theoretic*, 4.664; *observed*, 4.703; *Mol. Vol.*  $\square$ ; *Rel. wt.* 67.5; *Boiling-pt.*  $176^\circ.6$  ( $77^\circ \text{C.}$ )).—If equal measures of sulphurous anhydride and chlorine, both perfectly dry, be mixed together, no change occurs in diffused daylight, but under the influence of bright sunshine they unite and become condensed into a colourless liquid, with an extremely pungent odour, and an irritating effect upon the eyes. It may be obtained more easily by distilling an intimate mixture of phosphoric chloride or of phosphoryl chloride with plumbic sulphate; plumbic phosphate and sulphuryl chloride being formed (Carius); the reaction with the phosphoryl chloride being as follows;  $3\text{PbSO}_4 + 2\text{POCl}_3 = \text{Pb}_3\text{O}_4 + 3\text{SO}_2\text{Cl}_2$ . This substance ought not to be called an acid, for it does not form any peculiar class of salts. It may be distilled

unchanged from caustic lime or baryta; but by admixture with water it is immediately decomposed into sulphuric and hydrochloric acids;  $\text{SO}_2\text{Cl}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HCl}$ . An analogous compound ( $\text{SO}_2\text{I}_2$ ) may be formed with iodine. These bodies were considered by H. Rose and by Berzelius, as compounds of sulphuric anhydride with chloride or iodide of sulphur;  $3\text{SO}_2\text{Cl}_2 = 2\text{SO}_3\cdot\text{SCl}_2$ ; but they probably are to be regarded as bodies formed on the type of sulphuric anhydride, and containing 2 atoms of chlorine or of iodine in place of the third atom of oxygen. By transmitting the vapours of sulphuric anhydride into chloride of sulphur cooled by a freezing mixture, Rose obtained a fuming, oily-looking compound ( $\text{SO}_3\cdot\text{SO}_2\text{Cl}_2$ ; *sp. gr. of liquid*, 1.818; *of vapour*, 4.481, which boils at  $293^\circ$  ( $145^\circ\text{C}$ ).

(425) NITROSULPHURIC ACID ( $\text{H}_2\text{SO}_3\cdot 2\text{NO} = 142$ ) is not known in the form of the free acid.—Nitric oxide and sulphurous anhydride may be mixed with each other in a dry state without entering into combination, but if a strong solution of potash be thrown up into a jar containing a mixture of 2 volumes of nitric oxide and 1 volume of sulphurous anhydride, over mercury, the gas is gradually and completely absorbed. If a concentrated solution of ammonia be saturated with sulphurous acid, then mixed with four or five times its bulk of the solution of ammonia, and a current of nitric oxide be slowly transmitted, whilst the liquid is artificially kept cool, the gas is in great measure absorbed, and beautiful snow-white rhombic crystals of ammonic nitrosulphate [ $(\text{H}_4\text{N})_2\text{SO}_3\cdot 2\text{NO}$ ] are deposited; they may be collected on a filter, washed with a little ice-cold solution of ammonia, and dried *in vacuo* over sulphuric acid.

This salt is a singularly unstable compound; when dissolved in water it begins to undergo decomposition at ordinary temperatures: the presence of a free alkali increases its stability. If an attempt be made to liberate the acid by the addition of another acid to the salt, brisk effervescence, due to the escape of nitrous oxide, takes place, and sulphuric acid remains in the liquid,  $\text{H}_2\text{SO}_3\cdot 2\text{NO}$  giving  $\text{H}_2\text{SO}_4 + \text{N}_2\text{O}$ . Mere admixture of the solution of the ammonic nitrosulphate with that of many metallic salts, such for instance as cupric sulphate, produces a similar decomposition: probably a double decomposition occurs;  $\text{CuSO}_4 + (\text{H}_4\text{N})_2\text{SO}_3\cdot 2\text{NO}$  becoming  $(\text{H}_4\text{N})_2\text{SO}_4 + \text{CuSO}_3\cdot 2\text{NO}$ , whilst the cupric nitrosulphate is immediately resolved into nitrous oxide and cupric sulphate. If the dry ammonic nitrosulphate be heated a little above  $230^\circ$  ( $115^\circ\text{C}$ ), it is decomposed with explosive evolution of nitrous oxide.

The potassic and sodic nitrosulphates are rather more stable. No insoluble nitrosulphates have been formed; they give no precipitate with baryta water. The nitrosulphates of the alkali-metals are neutral to test-paper, and have a pungent bitterish taste.

(426) *Compounds of Sulphurous and Nitrous Acids; Sulphazotised Acids of Fremy*.—A remarkable series of salts has been described by Fremy (*Ann. de Chimie*, III. xv. 408), formed by the action of sulphurous anhydride upon a solution of potassic nitrite containing a large excess of free alkali. Sulphurous anhydride combines with the elements of potassic nitrite and water in several different proportions, and forms compounds which crystallize readily, and in which neither a sulphite nor a nitrite can be detected by the usual tests. The solutions of these salts produce, in solutions of salts of barium, a precipitate which contains the new acid. These compounds are all decomposed by boiling their solutions, and ammonia and sulphuric acid are amongst the products: some of them even experience a similar decomposition at ordinary temperatures.

The subjoined formulæ will sufficiently indicate the derivation of these salts from potash, water, nitrous and sulphurous anhydrides:—

Potassic sulphazite	$3K_2O, S_3N_2H_6O_{12}$ or $3K_2O + N_2O_3 + 3SO_2 + 3H_2O$
„ sulphazate	$3K_2O, S_4N_2H_6N_{14}$ or $3K_2O + N_2O_3 + 4SO_2 + 3H_2O$
„ sulphazotate	$3K_2O, S_5N_2H_6O_{16}$ or $3K_2O + N_2O_3 + 5SO_2 + 3H_2O$
„ sulphammonate	$4K_2O, S_8N_2H_6O_{22}$ or $4K_2O + N_2O_3 + 8SO_2 + 3H_2O$

It is remarkable that if sodic nitrite be substituted for potassic nitrite, no sulphazotised salts are formed. Indeed, Fremy was unable to procure any such compound which contained sodium.

Potassic sulphammonate is easily formed by mixing a strong solution of potassic sulphite with one of potassic nitrite; the sulphammonate is deposited in beautiful silky needles.

### COMPOUNDS OF SULPHUR WITH HYDROGEN.

(427) **HYDROSULPHURIC ACID; Dihydric Sulphide; Sulphuretted Hydrogen;**  $H_2S = 34$ ; *Mol. Vol.*  $\square$ ; *Rel. wt.* 17; *Theoretic Sp. Gr.* 1.174; *Observed*, 1.1912.—Sulphur forms with hydrogen an important compound commonly termed sulphuretted hydrogen, but which, as it possesses feebly acid properties is sometimes called hydrosulphuric acid. It is formed in small quantities when sulphur is heated in hydrogen gas, but it is always prepared for use by decomposing one of the metallic sulphides with an acid.

*Preparation.*—1. For ordinary purposes, about half an ounce (15 grms.) of ferrous sulphide ( $FeS$ ), in small fragments, is placed in a bottle, and is decomposed in the cold by an ounce (about 30 cub. centim.) of sulphuric acid diluted with 6 or 8 times its bulk of water; gas is immediately formed in abundance: the iron and hydrogen change places, ferrous sulphate is dissolved in the act of formation, and sulphuretted hydrogen is evolved;  $FeS + H_2SO_4 = H_2S + FeSO_4$ . The gas which is procured in this manner is commonly contaminated with free hydrogen, because the ferrous sulphide often contains a portion of metallic iron disseminated through it.

Fig. 315 shows a convenient method of mounting an apparatus for disen-

Fig. 315.

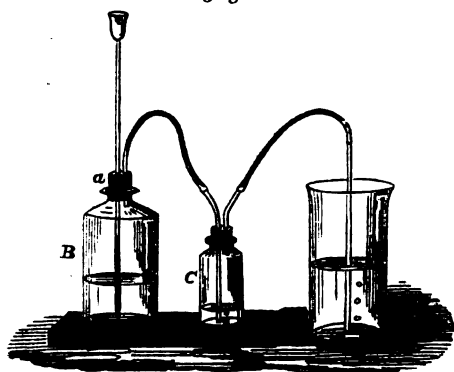
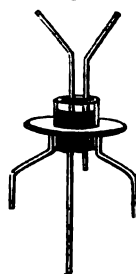


Fig. 316.



gaging a continuous current of the gas from ferrous sulphide. The cork through which the tubes pass is not fitted at once into the bottle, B or C, but is made to fit, as at *a*, into a piece of stout glass tube, open at both ends, such as is shown in fig. 316; this tube is ground so as to close the neck of the bottle air-tight, like an ordinary stopper. The apparatus, which requires to be frequently dismounted in order to be charged afresh, may thus be kept in a serviceable condition without the trouble or loss of time consequent on the frequent renewal of the corks, which would be needed unless this expedient were adopted. The various small tubes are connected together by long pieces of vulcanized caoutchouc tubing.

2.—When the gas is required in a state of purity, 1 part of powdered antimonious sulphide is substituted for the ferrous sulphide: in this case it is necessary to employ 3 or 4 parts of hydrochloric acid of sp. gr. 1.17, and to apply a gentle heat to the mixture; the apparatus may then be arranged as in fig. 317. In either case the gas requires to be washed before collecting it, in order to remove any particles of the acid or of the metallic salt which may have been carried over with it in mechanical suspension. As the compound of antimony with sulphur is a sesquisulphide ( $\text{Sb}_2\text{S}_3$ ), 1 atom of it requires 6 atoms of hydrochloric acid for its decomposition, and furnishes 2 atoms of antimonious chloride and 3 of sulphuretted hydrogen;  $\text{Sb}_2\text{S}_3 + 6\text{HCl} = 2\text{SbCl}_3 + 3\text{H}_2\text{S}$ .

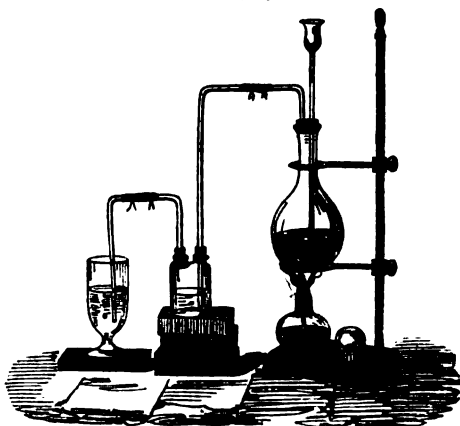


FIG. 317.

*Properties.*—Hydrosulphuric acid is a transparent colourless gas, of a disgusting odour, resembling that of rotten eggs. It is highly poisonous when respired in a concentrated form, and even when diluted with from 600 to 1200 times its bulk of air is rapidly fatal to the lower animals. It is inflammable, and burns with a pale, bluish flame, depositing sulphur if the supply of air be insufficient for complete combustion. If transmitted through tubes heated to full redness, it is partially decomposed into sulphur and free hydrogen. Its density a little exceeds that of atmospheric air, 1 litre at  $0^\circ \text{C}$ . 760<sup>mm</sup>. Bar. weighing 1.5475 grm. or 100 cub. in., weighing at  $60^\circ$  and 30 inches rather more than 38 grains.

*Composition.*—The proportion of hydrogen in a given volume of the gas may be ascertained by heating some granulated tin in a small retort filled with sulphuretted hydrogen and inverted in a vessel of mercury: the sulphur combines with the tin, whilst the hydrogen which remains occupies when cold the same space as

the gas before it was decomposed.\* In sulphuretted hydrogen, 1 volume of sulphur vapour and 2 volumes of hydrogen are therefore condensed into the space of 2 volumes, and the composition of the gas may be thus represented :—

		By weight.		By vol.		Sp. gr.
Sulphur ...	S	= 32	or 94'12	1	or 0'5	= 1'105
Hydrogen...	H <sub>2</sub>	= 2	5'88	2	1'0	= 0'069
		<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	H <sub>2</sub> S	= 34	100'00	2	1'0	= 1'174

Sulphurous anhydride and sulphuretted hydrogen, in the presence of moisture, decompose each other, half the oxygen of the sulphurous anhydride uniting with the hydrogen of the sulphuretted hydrogen, water and pentathionic acid (423) being formed whilst sulphur is deposited. For complete decomposition, equal volumes of sulphuretted hydrogen and of sulphurous anhydride would be requisite;  $10\text{SO}_2 + 10\text{H}_2\text{S} = 5\text{S}_2 + 8\text{H}_2\text{O} + 2\text{H}_2\text{S}_5\text{O}_6$ . Much of the sulphur thus deposited is in the electro-positive form (408), and is insoluble in carbonic disulphide. It is probable that a large proportion of native sulphur has been deposited from the gaseous form in consequence of this reaction.

Hydrosulphuric acid is also immediately decomposed by chlorine, bromine, and iodine; sulphur being precipitated, and hydrochloric, hydrobromic, or hydriodic acid being formed by the union of the hydrogen with one of the halogens above mentioned.

Under a pressure of about 17 atmospheres, sulphuretted hydrogen is reducible to a colourless, extremely mobile liquid, which, according to Regnault, boils at  $-79^{\circ}6$  ( $-62^{\circ}$  C.); it freezes to a transparent mass at a temperature of  $-122^{\circ}8$  ( $-86^{\circ}$  C.)

Water at  $32^{\circ}$  dissolves 4'37 times its bulk of sulphuretted hydrogen; 3'23 times its bulk at  $59^{\circ}$ , and 2'66 at  $75^{\circ}2$  ( $24^{\circ}$  C.) (Bunsen). The solution is feebly acid, and has the smell and taste of the gas. When exposed to the air, this solution becomes turbid; the hydrogen is slowly oxidized, forming water, and the sulphur is separated. If the oxidation of sulphuretted hydrogen takes place in a moist atmosphere, a little sulphuric acid is formed, and this action is favoured by the presence of a base to combine with the newly-formed acid.

Sulphuretted hydrogen is formed spontaneously under a variety of circumstances. Whenever a soluble sulphate remains in contact with decaying animal or vegetable matter, the sulphate

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\* Potassium cannot be employed instead of tin in this case, because, though it decomposes the gas, the dipotassic sulphide which is formed enters into combination with another portion of the gas without decomposing it.

loses oxygen, which combines with the elements of the decaying substance, whilst sulphide of the metal remains; one atom of calcic sulphate, for example, by the abstraction of 4 atoms of oxygen, becomes converted into calcic sulphide; thus  $\text{CaSO}_4 - 2\text{O}_2 = \text{CaS}$ .

In this way soluble sulphides are formed in many springs, such as those of Harrogate, giving to them their peculiar sulphureous odour: and, in a somewhat similar manner, sulphuretted hydrogen is generated in large quantities in stagnant sewers and cesspools.

The sulphides thus formed are readily decomposed by acids—even the carbonic acid absorbed from the atmosphere being sufficient to cause the expulsion of sulphuretted hydrogen, and in this way to occasion the odour observed on exposing such compounds to a damp air.

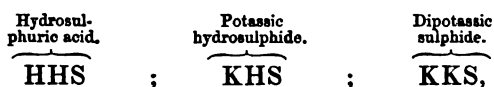
(428) *Hydrosulphates, or Sulphides*.—Hydrosulphuric acid, though a feeble acid, combines readily with bases: for example, if the gas be transmitted into a solution of potash or solution of ammonia, it is rapidly absorbed,—hydrosulphate of potash,  $\text{K}_2\text{O}, \text{H}_2\text{S}$ , or hydrosulphate of ammonia,  $(\text{H}_3\text{N})_2\text{H}_2\text{S}$ , being formed. Such solutions are, however, generally regarded as containing sulphides of the metals, because the hydrogen of the acid is exactly equivalent to the oxygen of the base, and is capable, as in the analogous case of the chlorides, of forming water and a metallic sulphide: for example, hydrosulphate of potash ( $\text{K}_2\text{O}, \text{H}_2\text{S}$ ) may be regarded as dipotassic sulphide and water, or as  $\text{K}_2\text{S} + \text{H}_2\text{O}$ . Moreover, the action of sulphuretted hydrogen in cases in which it occasions a precipitate in the solution of a metallic salt, consists in the formation of an insoluble metallic sulphide: when, for instance, cupric sulphate in solution is treated with sulphuretted hydrogen, an abundant black precipitate of hydrated cupric sulphide is produced, water is formed, and the liquid becomes acid from the liberation of sulphuric acid:  $\text{CuSO}_4 + \text{H}_2\text{S} + x\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{CuS}, x\text{H}_2\text{O}$ . The larger number of the metallic sulphides when thus formed combine with water at the moment of their precipitation.

Sulphuretted hydrogen is in continual requisition in the laboratory as a test for the discovery of metallic bodies: it gives characteristic precipitates with many metallic salts; for instance, with the compounds of lead it gives a black, with those of arsenicum, a yellow, and with those of antimony an orange-coloured precipitate. Many metallic solutions, such as those of zinc, iron, and manganese, when acidulated, yield no precipitate with

it: and it is therefore commonly employed, in the course of analysis, to separate these metals from others which are thrown down by it in the form of insoluble sulphides. For this purpose a current of the gas is transmitted through the solution on which it is designed to act. In these cases it is always necessary to purify it from particles held in mechanical suspension, and carried over by the effervescence of the materials employed; it is therefore first allowed to bubble up through a layer of water in a Woulfe's bottle interposed between the generator and the liquid to be submitted to its action, as shown at *c*, fig. 315.

When in any salt the attraction between the metal and the salt-radicle is too great to be overcome by the action of hydrosulphuric acid, the sulphide may notwithstanding be obtained, provided that an alkali-metal be simultaneously presented to the salt-radicle; this may easily be effected by mixing a soluble sulphide with the salt to be decomposed:—if ferrous sulphate ( $\text{FeSO}_4$ ) be exposed to a current of sulphuretted hydrogen it will experience no change; but if mixed with a solution of dipotassic sulphide, a black precipitate of hydrated ferrous sulphide ( $\text{FeS}, x\text{H}_2\text{O}$ ) is immediately produced, while potassic sulphate is formed in the solution:  $\text{FeSO}_4 + \text{K}_2\text{S}, x\text{H}_2\text{O} = \text{K}_2\text{SO}_4 + \text{FeS}, x\text{H}_2\text{O}$ . The sulphides thus formed are very commonly hydrated compounds: when exposed to the air in their moist condition, many of them absorb oxygen rapidly; solutions of the alkaline sulphides have indeed been employed for absorbing oxygen from gaseous mixtures. The results of oxidation vary, some being converted, like nickel sulphide into sulphate;  $\text{NiS}, x\text{H}_2\text{O} + 2\text{O}_2 = \text{NiSO}_4 + x\text{H}_2\text{O}$ : whilst others are simply converted, like ferrous sulphide, into free sulphur and the metallic oxide;  $4\text{FeS}, x\text{H}_2\text{O} + 3\text{O}_2$  becoming  $2\text{Fe}_2\text{O}_3, x\text{H}_2\text{O} + 2\text{S}_2$ .

Hydrosulphuric acid is usually stated to have a strong disposition to combine with the soluble sulphides, to form definite compounds with them. These compounds, however, are most easily represented by regarding them as double sulphides of the metal and hydrogen, intermediate between the hydrosulphuric acid and the ordinary sulphide—*e.g.*:—



corresponding with the compounds in the oxygen series indicated by the formulæ:—



To this class of double sulphides belongs the ordinary test-liquid ( $\text{H}_4\text{NHS}$ ), ammoniac hydrosulphide, which is used in the laboratory under the name of hydrosulphate of ammonia. These compounds emit a strong odour of sulphuretted hydrogen, and when decomposed by a metallic salt, the hydrosulphuric acid is set at liberty; for example;  $2\text{H}_4\text{NHS} + \text{MnSO}_4 = (\text{H}_4\text{N})_2\text{SO}_4 + \text{MnS} + \text{H}_2\text{S}$ . This evolution of sulphuretted hydrogen distinguishes them from the simple sulphides. No such double sulphides are formed with hydrogen and the dyads or tetrads, such as the metals of the earths proper and of the iron group.

*Tests.*—Many of the hydrosulphates and sulphides are easily detected by the odour of sulphuretted hydrogen which they evolve when moistened with hydrochloric acid. A very minute trace of the gas may be detected by enclosing a piece of paper moistened with a solution of plumbic acetate in the upper part of the tube or vessel in which the suspected sulphide has been mixed with acid; if sulphuretted hydrogen be evolved, a brown or black tinge occurs upon the paper after the lapse of a few minutes, owing to the formation of plumbic sulphide. The proportion of free sulphuretted hydrogen, or of a soluble sulphide in any solution, may be accurately determined by mixing the liquid to be tested with a small quantity of a cold solution of starch slightly acidulated with acetic acid, and adding a standard solution of iodine dissolved in potassic iodide until the starch assumes a blue tint from the action of excess of iodine; in this reaction the sulphuretted hydrogen converts the iodine into hydriodic acid, whilst the liquid becomes turbid from the separation of sulphur;  $2\text{H}_2\text{S} + 2\text{I}_2 = 4\text{HI} + \text{S}_2$ .

Traces of soluble sulphides may be detected in neutral or alkaline solutions by the magnificent purple colour which they form on the addition of a solution of sodic nitroprusside. When heated before the blowpipe, most of the sulphides emit the odour of sulphurous anhydride (535, 536).

(429) **HYDRIC PERSULPHIDE**, or *Persulphide of Hydrogen* ( $\text{H}_2\text{S}_2$ ? or  $\text{H}_2\text{S}_4$ ?); *Sp. Gr. of Liquid*, 1.769.—In order to procure this compound it is usual to begin by preparing a calcic pentasulphide ( $\text{CaS}_5$ ), which may be obtained by boiling equal weights of slaked lime and powdered sulphur in water; calcic pentasulphide mixed with a corresponding amount of calcic hyposulphite is formed, and enters into solution;  $3\text{CaOH}_2\text{O} + 6\text{S}_2 = \text{CaS}_5\text{H}_2\text{O}_4 + 2\text{CaS}_2 + 2\text{H}_2\text{O}$ : the undissolved sulphur is separated by filtration. On allowing the deep yellow liquid to fall into hydrochloric acid diluted with twice its bulk of water, and gently warmed, hydric persulphide subsides as an oily liquid, having a smell and



taste resembling that of hydrosulphuric acid : it burns with a blue flame. In many of its properties it presents a striking analogy with hydric peroxide (485); it possesses bleaching powers, is very prone to spontaneous decomposition into sulphur and sulphuretted hydrogen; it is rendered more stable by the presence of acids, and is immediately decomposed by alkalies. The latter circumstance renders it necessary in preparing this compound to add the calcic pentasulphide to the acid, not the acid to the pentasulphide, which would be attended with an escape of hydrosulphuric acid and a precipitation of finely divided sulphur. The sulphur which is precipitated in this manner from an alkaline pentasulphide was formerly employed in medicine under the term of *lac sulphuris*.

Oxides of manganese and silver decompose hydric persulphide by mere contact with the liquid, producing a violent effervescence, owing to the disengagement of sulphuretted hydrogen. Hydric persulphide dissolves sulphur freely, and hence its composition is not certainly known, since a portion of sulphur derived from the calcic hyposulphite formed in preparing the pentasulphide is always precipitated along with the persulphide, and becomes dissolved in the liquid obtained, which, owing to its instability, cannot be purified by distillation.

(430) CARBONIC DISULPHIDE, or *Bisulphide of Carbon*; *Sulpho-carbonic Acid* ( $\text{CS}_2 = 76$ ); *Sp. Gr. of Liquid*, 1.272 at  $60^\circ$  ( $15^\circ.5 \text{ C.}$ ); *of Vapour, Theoretic*, 2.626; *Observed*, 2.6447; *Mol. Vol.*   ; *Rel. wt.* 38; *Boiling-pt.*  $118^\circ.4$  ( $48^\circ \text{ C.}$ ).—This compound may be prepared by heating fragments of charcoal to bright redness in an earthen retort, furnished with a tubulure into which is luted a porcelain tube, passing nearly to the bottom of the retort: the tube is provided at its upper extremity with a cork. From time to time this cork is withdrawn, and a fragment of sulphur is dropped into the retort; the cork is then immediately replaced, the sulphur melts, and is converted into vapour; at this elevated temperature the carbon combines with it, and the disulphide thus obtained may be condensed in vessels properly cooled. It is now manufactured on a very large scale, both in this country and in France, by the use of suitable apparatus constructed on this principle, the vapour of sulphur being driven over glowing coke. It is yellow when first formed, and contains an excess of sulphur; but by redistillation it may be obtained in a state of purity. It is a very volatile, colourless liquid, of high refracting power, of an acrid, pungent taste, and a foetid, peculiar, sulphurous odour. It is heavier than water, in which it is insoluble, but it is soluble in all proportions in ether and in alcohol, in benzol, in oil of turpentine, as well as in the fixed and volatile oils. Disulphide of carbon has never hitherto been frozen; hence it has been employed sometimes in the construction of thermometers destined to measure very intense degrees of cold.

The vapour of carbonic disulphide when breathed produces great depression followed by coma. It is indeed very poisonous, and hence much care is requisite in preventing its escape into the

apartments in which the work-people are engaged. It produces in those more or less exposed to its fumes, depression, weakness, and loss of memory ; for the relief of these symptoms the use of a solution of ferrous carbonate in carbonic acid water has been found in some degree effectual. Advantage has been taken of this poisonous property to free grain infested with weevils from the insect ; a small quantity of the disulphide enclosed in a tight chamber with the grain, in a few hours kills both the larvæ and the eggs (Doyère), and does not injure the grain ; on exposure to air the disulphide quickly evaporates. Indeed, the applications of the disulphide in the arts are very numerous, and are of growing importance.

Carbonic disulphide is highly inflammable, when its vapour is mixed with hydrogen or carbonic oxide it takes fire below  $420^{\circ}$  ( $215^{\circ}.5$  C.) (Frankland) ; in consequence of which when used it requires special precautions against fire. It burns with a blue flame, producing gaseous sulphurous and carbonic anhydrides. It dissolves sulphur freely, and, by spontaneous evaporation, leaves it in rhombic octohedra. Phosphorus is also freely dissolved by it, and may be obtained in crystals from the solution by slow evaporation. Iodine, bromine, and chlorine are likewise readily dissolved by the disulphide. It is one of the best solvents of caoutchouc ; it may be substituted for ether as a solvent for some of the organic bases, and it has been used on a very large scale by Deiss as a solvent for extracting oils and fats, as, for example, in economizing the last portions of olive oil left in the pulp of the fruit after pressure. It has also been used as a solvent for extracting bitumen from minerals which contain it, instead of subjecting them to the ordinary process of destructive distillation ; and it has been employed as a solvent in the analysis of oil seeds, for the purpose of ascertaining the proportion of oil which the ground seeds contain (*Richardson and Watts' Technology*, vol. i. Part III. p. 138).

Carbonic disulphide offers one of the best illustrations of the analogy in properties between oxygen and sulphur ; an analogy which, though far from being so complete as that of the different halogens with each other, is yet in some respects of a striking character. It is to be remarked that sulphur is the only non-metallic element excepting oxygen with which carbon can be easily caused to unite directly. The compound of carbon and sulphur so obtained affords a good instance of the class of combinations which Berzelius has called *sulphur-acids*, these substances possessing the power of uniting with the sulphides of the

basic metals, and forming with them *sulpho-salts*, corresponding in composition to analogous salts which contain oxygen:—Carbonic disulphide, for example, may be regarded as the analogue of carbonic anhydride; it contains 2 atoms of sulphur in the place of 2 atoms of oxygen, the composition of the compound being the following:—

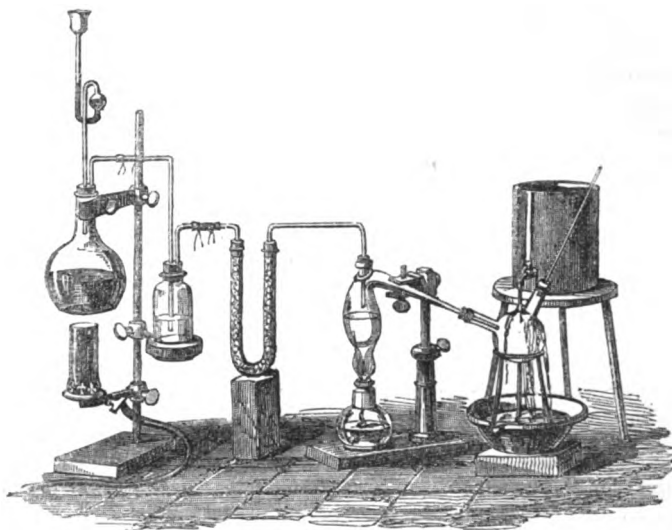
		By weight.		By vol.		Sp. gr.
Carbon ...	C =	12	or 15.79	2 ?	or 1.0	0.4146
Sulphur ...	S <sub>2</sub> =	64	84.21	2	1.0	2.2114
<hr/>						
Carbonic disulphide } CS <sub>2</sub>		76	100.00	2	1.0	2.6260

Carbonic disulphide combines with the sulphides of the alkali-metals, forming a species of salts which are called *sulpho-carbonates*, such for instance as potassic sulpho-carbonate (K<sub>2</sub>CS<sub>3</sub>), which contains 3 atoms of sulphur in the place of the 3 atoms of oxygen in the corresponding carbonate, K<sub>2</sub>CO<sub>3</sub>. The soluble sulpho-carbonates are easily converted, by boiling their aqueous solutions, into carbonate of the metal; water being decomposed, whilst an evolution of sulphuretted hydrogen takes place; for example: K<sub>2</sub>CS<sub>3</sub> + 3H<sub>2</sub>O = K<sub>2</sub>CO<sub>3</sub> + 3H<sub>2</sub>S; and a similar decomposition takes place slowly in the aqueous solution at ordinary temperatures. The sulpho-carbonates when decomposed by hydrochloric acid form a yellow oily liquid, containing the elements of carbonic disulphide and sulphuretted hydrogen; for instance, K<sub>2</sub>CS<sub>3</sub> + 2HCl = H<sub>2</sub>CS<sub>3</sub> + 2KCl. Solutions of the sulpho-carbonates of the alkali-metals give a brown precipitate with solutions of the salts of copper: they yield, with dilute solutions of argentic nitrate and of corrosive sublimate, yellow precipitates; and with lead salts they give a red precipitate. All these precipitates blacken, more or less speedily, when kept, owing to their conversion into sulphides. Aqueous solutions of the hydrated alkalis gradually discolour the disulphide, and form a brown liquid containing carbonate and sulpho-carbonate of the metal; for example, 6KHO + 3CS<sub>2</sub> = K<sub>2</sub>CO<sub>3</sub> + 2K<sub>2</sub>CS<sub>3</sub> + 3H<sub>2</sub>O.

(431) SULPHUR CHLORIDE (S<sub>2</sub>Cl<sub>2</sub> = 135); *Mol. Vol.*  ; *Rel. wt.* 67.5; *Sp. Gr. of Liquid*, 1.68; *of Vapour*, 4.70; *Boiling-pt.* 280° 4 (138° C.).—Chlorine and sulphur form two compounds with each other; they combine gradually at common temperatures, but if heated together the union is rapid. In preparing the chloride (S<sub>2</sub>Cl<sub>2</sub>) the arrangement shown in fig. 318 may be adopted, in which a steady current of washed and dried chlorine is directed towards the bottom of a retort containing melted sulphur; the resulting chloride must be collected in a perfectly dry receiver,

kept cool: it may be purified from excess of chlorine by redistillation from powdered sulphur; a yellow volatile liquid, of pene-

FIG. 318.



trating, peculiar, and disagreeable odour is thus formed. It emits fumes on exposure to the air, owing to its action on the atmospheric moisture. When dropped into water it falls to the bottom, and is slowly decomposed into hydrochloric and sulphurous acids, mixed with some of the polythionic acids, and free sulphur in the electro-positive form. It acts powerfully on mercury when brought into contact with it, and dissolves sulphur freely; with ammonia it combines in two proportions, forming the compounds  $2\text{H}_3\text{N}$ ,  $\text{S}_2\text{Cl}_2$ , and  $4\text{H}_3\text{N}$ ,  $\text{S}_2\text{Cl}_2$ . An oxychloride of sulphur ( $\text{S}_2\text{Cl}_4\text{O}_3$ )\* is

\* Two other oxychlorides of sulphur are also known, one the *thionyl chloride* ( $\text{SOCl}_2$ ) corresponding to sulphurous anhydride in which one-half of the oxygen is displaced by chlorine. It is a colourless liquid, which boils at  $179^\circ\text{C}$ . ( $82^\circ\text{C}$ .) and is obtained by decomposing phosphoric chloride by means of dry sulphurous anhydride. The other compound has already been described under the name of chlorosulphuric acid ( $\text{SO}_2\text{Cl}_2$ ), or *sulphuryl chloride* (424), corresponding to sulphuric anhydride in which an atom of oxygen has been displaced by its equivalent (2 atoms) of chlorine.

These oxychlorides of sulphur and Williamson's chlorhydro-sulphuric acid (416) form a series, some relations of which will be rendered evident by writing their formulæ as follows:—

Thionyl chloride	...	...	...	...	$\text{S}_2\text{O}_2\text{Cl}_4$
Crystalline oxychloride	...	...	...	...	$\text{S}_2\text{O}_2\text{Cl}_4$
Sulphuryl chloride	...	...	...	...	$\text{S}_2\text{O}_2\text{Cl}_4$
Rose's oxychloride	...	...	...	...	$\text{S}_2\text{O}_2\text{Cl}_4$
Chlorhydro-sulphuric acid	...	...	...	...	$\text{S}_2\text{O}_2\text{H}_2\text{Cl}_4$

obtained in crystals by transmitting moist chlorine through the chloride.

*Sulphur dichloride* ( $\text{SCl}_2 = 103$ ; *Sp. Gr. of Liquid*, 1.625) may be formed by saturating the preceding compound with chlorine: it is a deep-red liquid, which fumes strongly in the air, and is decomposed in the direct rays of the sun into the chloride  $\text{S}_2\text{Cl}_4$  and free chlorine. It is partially decomposed by boiling it. Carius, in his elaborate examination of these compounds (*Liebigs Annal.* cvi. 291), even denies its existence as a separate body, regarding the red liquid as a mixture of the chloride  $\text{S}_2\text{Cl}_4$  with a higher chloride ( $\text{SCl}_3$ ) not yet isolated.

The *bromides* of sulphur are liquids analogous to the chlorides. The *iodide* ( $\text{S}_2\text{I}_2$ ) is a crystalline, brittle, steel-grey solid; but the compound is unstable, and gradually loses iodine by exposure to the air.

(432) NITROGEN SULPHIDE ( $\text{SN}$ ; Fordos and Gélis, *Ann. de Chimie*, III. xxxii. 389).—This compound is obtained, though in small quantity only, when sulphur chloride is dissolved in 10 or 12 times its bulk of carbonic disulphide and decomposed by a current of dry ammoniacal gas. The gas is transmitted till the brown colour of the precipitate which is formed disappears; the yellow liquid is filtered from the sal ammoniac, and left to spontaneous evaporation; beautiful golden yellow rhombic crystals of nitrogen sulphide, mixed with crystals of sulphur, are speedily formed; the sulphur may be removed by digestion in cold carbonic disulphide. The reaction which attends its formation is very complicated, and has not been completely ascertained. Nitrogen sulphide detonates powerfully by percussion, and explodes when heated to  $314^{\circ}\cdot6$  ( $157^{\circ}\text{C}$ ). It has a faint odour, adheres strongly to paper if rubbed on it, and irritates the mucous membrane of the eyes and nose most painfully. Carbonic disulphide takes up about  $\frac{1}{300}$  of its weight when boiled upon it; alcohol, ether, and oil of turpentine dissolve it very sparingly; water does not dissolve it, but slowly decomposes the compound. Nitrogen sulphide combines with the chlorides of sulphur in several proportions.

## § II. SELENIUM ; $\text{Se} = 79\cdot5$ .

*Theoretic Sp. Gr. of Vapour*, 5.526 ; *Observed at*  $2588^{\circ}$  ( $1420^{\circ}\text{C}$ )., 5.68 ; *Atomic Vol.*  $\square$  ; *Rel. wt.* 79.5 ; *Sp. Gr. Cryst.* 4.788 : usually Dyad, as in  $\text{H}_2\text{Se}$  ; occasionally Tetrad, as in  $\text{SeCl}_4$  ; *Mol. Vol. of Vapour* ( $\text{SeSe}$ ) =  $\square\square$  ; *Mol. wt.* = 159.

(433) SELENIUM is a mythological name (from  $\sigma\epsilon\lambda\acute{\eta}\nu\eta$ , the moon) given by Berzelius to a rare elementary body, discovered by him during the year 1817, in the refuse of a sulphuric acid manufactory near Fahlun. It derives its chief interest from the remarkable analogy to sulphur which it presents. Selenium always occurs in combination ; the compounds which it forms are termed *selenides*. The native selenides are very rare minerals, the most abundant of them being the selenides of iron, copper, and silver.

*Extraction*.—In order to obtain selenium in an isolated form, the Fahlun selenium residue is mixed with nitrate and carbonate of potassium, and deflagrated ; that is to say, the mixture is thrown in small quantities at a time into a red-hot crucible, in

which it burns vividly. The selenium and other bodies with which it is associated are oxidized at the expense of the oxygen of the nitre, whilst potassic seleniate is produced by acting on the disengaged potash of the nitre. The mass is digested in water, acidulated with hydrochloric acid, and evaporated down to a small bulk: the selenic acid is thus reduced to selenious acid;  $2\text{HCl} + \text{H}_2\text{SeO}_4 = \text{Cl}_2 + \text{H}_2\text{O} + \text{H}_2\text{SeO}_3$ : and the selenious acid, when treated with sulphurous acid, yields a precipitate of reduced selenium as a red, flocculent, amorphous powder;  $2\text{H}_2\text{SeO}_3 + 4\text{H}_2\text{SO}_3 = \text{Se}_2 + 4\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ .

*Properties.*—Selenium may be obtained in the amorphous, in the vitreous, and in the crystalline condition. When collected and dried, the pulverulent selenium begins to soften at a temperature below that of boiling water, and at a few degrees above  $212^\circ$  ( $100^\circ$  C.) it melts; on cooling, it forms a brittle solid, with glassy fracture, metallic lustre, and deep brown colour, varying in specific gravity from 4.3 to 4.8. It has neither taste nor smell; it is insoluble in water, and is a non-conductor of heat and of electricity. It is soluble in oil of vitriol, forming a green solution which, when diluted, deposits unaltered selenium. When melted it is ductile, and may be drawn out into fine threads.

The statements regarding its point of fusion are discordant, owing to its power of existing, like sulphur, in several distinct modifications. If it be maintained for some hours at  $200^\circ$  ( $93^\circ\text{3 C.}$ )—i.e. below its melting-point—the temperature suddenly rises till it reaches  $320^\circ$  ( $160^\circ$  C.), after which the selenium is found to have become granular and crystalline. The fusing-point of this variety is  $422^\circ\text{6}$  ( $217^\circ$  C.) (Hittorf.) It may also be obtained with some difficulty, crystallized in minute rhomboidal prisms of sp. gr. 4.5, from its solution in carbonic disulphide, which, at its boiling-point, dissolves about 1 per cent. of vitreous selenium. If these crystals be heated to about  $334^\circ$  ( $168^\circ$  C.), they become almost black, and increase in sp. gr. to 4.7, experiencing a molecular change, in consequence of which they are no longer soluble in carbonic disulphide; when this black mass is melted and quickly cooled, it resumes its solubility in this menstruum, owing to its reconversion into the vitreous condition.

When heated in the air, selenium does not readily take fire; it burns with a blue flame, but a portion of it is volatilized in red fumes, emitting an odour resembling that of carbonic disulphide; this is probably due to the formation of a protoxide of selenium, which, however, is not acid. If heated in closed vessels, selenium boils at a temperature below a red heat, and gives off a deep yellow vapour, which, according to Deville and Troost, is of sp. gr. 7.67 at  $1580^\circ$  ( $860^\circ$  C.); when heated to  $1904^\circ$  ( $1040^\circ$  C.) it has a sp. gr. of 6.37; while at  $2588^\circ$  ( $1420^\circ$  C.) it has a sp. gr. of 5.68 and has expanded, till, as in the case of sulphur, it occupies a bulk nearly equal to that of an equivalent of oxygen. The specific

gravity of selenium vapour calculated on the supposition that it exactly corresponds with the volume of an equivalent of oxygen is 5.526. The vapour condenses in red flowers or in opaque metallic-looking drops. Selenium forms with oxygen, two compounds, which when acted on by water, furnish acids; the first corresponding with sulphurous, and the second with sulphuric acid.

(434) SELENIOUS ANHYDRIDE, ( $\text{SeO}_2 = 111.5$ ; *Rel. wt.* 55.75; *Theoretic Sp. Gr. of Vapour*, 3.8419; *Observed*, 4.03; *Mol. Vol.*  $\square$ ), may be obtained by burning selenium in a current of oxygen, but it is usually prepared by boiling selenium with nitric acid or with aqua regia, by which the selenium is gradually oxidized and dissolved; the excess of nitric acid may be expelled by heat, leaving the selenious anhydride as a white mass, which does not melt on further urging the heat, but sublimes below redness, forming a yellow vapour, and condensing again in beautiful snow-white prismatic needles. The crystals are deliquescent; their aqueous solution is strongly acid, and it has a sour burning taste. *Selenious acid* ( $\text{H}_2\text{SeO}_3$ ) in solution is speedily deoxidized by iron or by zinc, either of which, when digested in the liquid, occasions the deposition of selenium in the form of a reddish-brown powder. A solution of sulphurous acid also readily reduces selenium from the acid.

*Selenites*.—Most of the selenites, except those of the metals of the alkalis, are insoluble in water, but soluble in nitric acid. With the alkali-metals three classes of salts may be formed: normal selenites, with the general formula  $\text{M}_2\text{SeO}_3$ , like disodic selenite,  $\text{Na}_2\text{SeO}_3$ ; acid selenites, with the general formula  $\text{MH}_2\text{SeO}_3$ , like hydrosodic selenite ( $\text{NaH}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ ); and hyperacid selenites, or quadri-selenites, with the general formula  $\text{MH}_2\text{SeO}_4$ , like trihydro-sodic selenite  $2(\text{NaH}_2\text{SeO}_4 \cdot \text{H}_2\text{O})$ . The selenites are easily recognized when heated on charcoal before the blowpipe in the reducing flame, by the peculiar odour of selenium which they emit; the selenites in solution, when treated with sulphurous acid, give a reddish-brown precipitate of reduced selenium.

(435) ~~SELENIC~~ ACID; *Dihydric selenate*;  $\text{H}_2\text{SeO}_4 = 145.5$ .—The anhydride of this acid is not known. The acid itself is best obtained in solution by deflagrating selenium or any selenite with nitre; the residue is dissolved in water, and mixed with a solution of plumbic nitrate; an insoluble plumbic selenate is precipitated, and this, if suspended in water, may be decomposed by a current of sulphuretted hydrogen. Plumbic sulphide is thus formed, and selenic acid is set at liberty;  $\text{PbSeO}_4 + \text{H}_2\text{S} = \text{H}_2\text{SeO}_4 + \text{PbS}$ . The acid may be separated by filtration, and concentrated by evaporation till it has a specific gravity of 2.6; if heated beyond  $554^\circ$  ( $290^\circ \text{C.}$ ) it is decomposed into selenious anhydride, water and oxygen. Selenic acid dissolves iron and

zinc with evolution of hydrogen; it also attacks copper and even gold, if boiled upon these metals, which are oxidized at the expense of the acid, selenious acid being disengaged; platinum is not attacked by it. Sulphurous acid is without effect upon selenic acid, but hydrochloric acid decomposes it when heated with it, chlorine and selenious acid being liberated;  $\text{H}_2\text{SeO}_4 + 2\text{HCl} = \text{H}_2\text{SeO}_3 + \text{H}_2\text{O} + \text{Cl}_2$ . Selenic acid closely resembles sulphuric acid in its properties, and its salts are isomorphous with the sulphates of the same metals.

*Seleniates.*—Selenic acid is dibasic. Solutions of the seleniates give white precipitates with salts of barium, strontium, and lead, owing to the formation of insoluble seleniates of these metals. These precipitates are insoluble in diluted nitric acid. When the soluble seleniates are boiled with hydrochloric acid, selenic acid is liberated, and is reduced to the form of selenious acid: sulphurous acid will then precipitate reduced selenium from the solution. Baric seleniate may be similarly decomposed, and may thus be distinguished from baric sulphate. When heated on charcoal before the blowpipe in the reducing-flame, the seleniates emit the characteristic odour of selenium.

(436) SELINIURETTED HYDROGEN; *Hydroselenic acid*; *Dihydric selenide*; ( $\text{H}_2\text{Se} = 81.5$ ); *Rel. wt.* 40.75; *Sp. Gr.* 2.795; *Mol. Vol.*  $\square$ .—This substance is a colourless inflammable gas, which resembles hydrosulphuric acid, but its odour is much more offensive. Berzelius found that by the application of the nose to a bubble of the gas no larger than a pea, he was deprived of the sense of smell for several hours. Seliniuretted hydrogen is obtained by acting on selenide of potassium or of iron, with diluted hydrochloric or sulphuric acid. This gas is soluble in water, and precipitates many metals from their salts in the form of selenides. Its solution has a feebly acid reaction; if exposed to the air it absorbs oxygen and deposits selenium. The selenides of the alkali-metals are soluble in water: those of cerium, zinc, and manganese, are flesh-coloured; most of the others are black.

(437) CHLORIDES OF SELENIUM.—Selenium unites directly with chlorine, forming two compounds, one a brownish volatile liquid ( $\text{Se}_2\text{Cl}_2$ ) heavier than water, and slowly decomposed by it; the other a volatile, white, crystalline mass ( $\text{SeCl}_4$ ), which is immediately decomposed by water into selenious and hydrochloric acids.

### § III. TELLURIUM: $\text{Te} = 129$ .

*Theoretic Sp. Gr. of Vapour*, 8.913; *Observed Sp. Gr. at 2534°* (1390° C.), 9.00; *Sp. Gr. of Solid*, 6.65; *Atomic Vol.*  $\square$ ; *Rel. wt.* 129; *Mol. Vol. of Vapour*,  $\square$ ; *Mol. wt.*,  $\text{Te}_2$ , 258; *usually Dyad, as in  $\text{H}_2\text{Te}$ : occasionally Tetrad, as in  $\text{TeCl}_4$ .*

(438) TELLURIUM is a rare substance discovered by Müller in 1782, but first investigated by Klaproth in 1798, and named by him from *tellus*, the earth. It is found chiefly in the mines of Hungary and Transylvania, occasionally native and nearly pure, but generally combined with various metals, such as gold, silver, bismuth, copper, or lead; it is usually also accompanied by small quantities of arsenicum and selenium. Its most common ore is



the black, foliated tellurium ore of Nagyag, which contains about 13 per cent. of tellurium in the form of tellurides of gold, lead, and silver, mixed with sulphides of antimony and lead. It may be extracted from this mineral by digestion of the finely-powdered ore in hydrochloric acid, which removes the sulphides of lead and antimony; the residue is washed and heated with nitric acid, the solution of tellurous nitrate is decanted, evaporated to dryness, and treated with hydrochloric acid, after which the tellurium is thrown down as a brown powder by the addition of sodic sulphite to the acid liquid. For additional particulars regarding the extraction of tellurium, the reader is referred to the *Lehrbuch* of Berzelius (German edition, 1844, vol. ii. p. 229).

*Properties.*—Most English writers on chemistry class tellurium amongst the metals. It presents, however, a close analogy with sulphur and selenium, though it possesses a high metallic lustre, and resembles bismuth in colour. It is very brittle, fuses between  $800^{\circ}$  and  $900^{\circ}$  ( $426^{\circ}$  and  $482^{\circ}$  C.), and at a high temperature it is converted into a yellow vapour which, according to Deville and Troost, has a density of 9.00 at a temperature of  $2534^{\circ}$  ( $1390^{\circ}$  C.). The distillation of tellurium is best conducted by heating it very strongly in a porcelain tube, and transmitting a current of dry hydrogen gas over it; the vapour of tellurium is thus mechanically carried forward, and it is condensed in drops and flexible crystalline needles in the cooler parts of the apparatus. According to Mitscherlich, tellurium, when solidified after fusion, exhibits a rhombohedral cleavage, a circumstance which seems to indicate its isomorphism with arsenicum and antimony. Tellurium is a bad conductor of heat and of electricity. When heated strongly in the air it takes fire, burns with a blue flame edged with green, and emits a peculiar characteristic odour, whilst thick white fumes of tellurous anhydride are produced. Like sulphur and selenium, tellurium is soluble in cold concentrated sulphuric acid, to which it gives a fine purple-red colour; on dilution it is precipitated unchanged. Minute quantities of tellurium, when taken internally, impart a persistent and intolerable odour of garlic to the breath.

Tellurium forms two oxides ( $\text{TeO}_2$ ;  $\text{TeO}_3$ ), which correspond in composition to sulphurous and sulphuric anhydrides.

(439) *Tellurous Acid* ( $\text{H}_2\text{TeO}_3 = 179$ ).—Tellurium is readily dissolved by nitric acid of sp. gr. 1.25. If the solution be poured into water immediately, a white, bulky hydrate of tellurous acid subsides. It is slightly soluble in water, reddens litmus, and combines with the alkaline bases; these compounds are soluble.

Tellurous acid has a bitter metallic taste: its anhydride may be obtained by gently heating the hydrate, or by boiling the nitric acid solution, when it is deposited in crystalline needles, which are very slightly soluble in water. The anhydride ( $\text{TeO}_2 = 161$ ; *Sp. Gr.* 5.93) fuses easily, forming a transparent glass, which is yellow while hot, but becomes white and crystalline on cooling. Tellurous anhydride possesses considerable volatility: if fused with caustic potash, potassic tellurite is formed.

Tellurites may be formed of three classes—normal salts,  $\text{M}_2\text{TeO}_3$ ; acid salts,  $\text{MHTeO}_3$ , and hyperacid salts, or quadritellurites,  $\text{MHTeO}_3 \cdot \text{H}_2\text{TeO}_3$ . The tellurites of the alkali-metals are soluble, those of the alkaline earths very sparingly so. This anhydride also, like many of the metallic anhydrides, combines with the stronger acids: the compounds which it thus furnishes have a metallic taste, and are said to act powerfully as emetics. Its salts with oxalic and tartaric acid are soluble. All the soluble salts in which tellurium acts as a basyl are decomposed if mixed with hydrochloric acid and heated with sulphurous acid: reduced tellurium is precipitated under these circumstances. With sulphuretted hydrogen a black sulphide of tellurium is produced.

(440) *Telluric Acid* ( $\text{H}_2\text{TeO}_4 = 195$ ) is obtained by gently heating tellurium or tellurous acid with nitre. A potassic tellurate is formed, from which the acid is transferred to barium, and the barium is separated by sulphuric acid. Telluric acid crystallizes in striated hexagonal prisms, which have a nauseous metallic taste; they exert but a feeble action on litmus. These crystals are composed of ( $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ ). If heated nearly to redness they furnish telluric anhydride, and then assume an orange-yellow colour. This anhydride ( $\text{TeO}_3 = 177$ ) is completely insoluble in water, and in nitric and hydrochloric acids, as well as in alkaline solutions.

Telluric acid has but a feeble chemical attraction for bases, but, like selenic acid, it forms three classes of salts which may be represented by the general formulæ,  $\text{M}_2\text{TeO}_4$ ;  $\text{MHTeO}_4$ ; and  $\text{MHTeO}_4 \cdot \text{H}_2\text{TeO}_4$ . Their solutions, when acidulated, yield a black precipitate with sulphuretted hydrogen. When telluric acid, or one of its salts, is heated to redness, oxygen is disengaged and the telluric is converted into tellurous anhydride, or the tellurate into a tellurite of the basyl.

Two *chlorides*,  $\text{TeCl}_3$  and  $\text{TeCl}_4$ , have been obtained by the direct action of chlorine upon tellurium: both of them are volatile; the vapour of the dichloride is of a violet colour; they are decomposed by a large quantity of water.

(441) *TELLURETTED HYDROGEN: Dihydric telluride*;  $\text{H}_2\text{Te} = 131$ ; *Sp. Gr.* 4.489; *Atomic and Mol. Vol.*   ; *Rel. wt.* 65.5.—The most interesting compound of tellurium is that which it forms with hydrogen. It is a gaseous body analogous to sulphuretted hydrogen, contains its own volume of hydrogen, and is possessed of feebly acid properties. It may be obtained by decomposing the alloy of tellurium with zinc or tin, by means of hydrochloric

acid. The gas which escapes burns with a blue flame; it reddens litmus, and has an odour which cannot be distinguished from that of sulphuretted hydrogen: with water it forms a colourless solution, which becomes brown by exposure to the air, owing to the oxidation of the hydrogen and separation of tellurium. Telluretted hydrogen precipitates most of the metals from their solutions, in the form of tellurides, which have a close analogy with the corresponding sulphides. The tellurides of the alkali-metals are soluble in water.

Tellurium, whether in the form of a soluble tellurite or in that of a tellurate, is thrown down from its solutions in the reduced form by zinc or iron; neutral solutions of the salts of both its acids are also reduced by ferrous sulphate and by stannous chloride; in these cases the tellurium falls in brown flocculi. The tellurates of the alkali-metals when heated to redness in a tube with charcoal are reduced to tellurides, which are soluble in water, and form a red liquid.

## CHAPTER VIII.

### § I. PHOSPHORUS: $P=31$ .\*

*Atomic Vol.*  $\square$ , or  $\frac{1}{2}$ ; *Rel. wt.* 62; *Theoretic Sp. Gr. of Vapour*, 4.284; *Observed Sp. Gr. of Vapour*, 4.42; *Fusing-pt.*  $111^{\circ}.5$  ( $44^{\circ}.2$  C.); *Boiling-pt.* about  $550^{\circ}$  ( $288^{\circ}$  C.); *usually Triad, as in  $H_3P$ ; frequently Pentad, as in  $PCl_5$ ; Mol. Vol.*  $\square\square\square$ ; *Mol. wt.*  $P_4=124$ .

(442) *Natural Relations of the Phosphorus Group.*—Phosphorus is described here for the sake of convenience, and not because it exhibits any relation to the sulphur group; it has, however, a close connexion with arsenicum and antimony, two bodies which will be described with the metals.

Phosphorus, arsenicum, and antimony afford good instances of the terequivalent or triad group of elements, as in most cases when in combination they represent 3 atoms of hydrogen, though sometimes they are quinquequivalent, or represent 5 atoms. These three elements are indeed related much in the same way as sulphur, selenium, and tellurium; each of them unites with hydrogen, and

\* The vapour volume of phosphorus appears to be tetratomic; for if the molecule of free phosphorus be taken as  $P_4$  it will furnish two volumes of vapour. Arsenicum resembles phosphorus in this respect.

forms a gaseous compound in which 3 volumes of hydrogen combine with  $\frac{1}{2}$  a volume of the vapour of the other element—the compound which is formed occupying the space of 2 volumes—these gaseous compounds exhibiting a tendency to alkalinity. Each of these elements unites with oxygen in the proportion of 2 atoms with 3, and 2 with 5 atoms of oxygen, forming compounds in which the acid character is less and less marked as the atomic weight of the combustible element increases. The isomorphous relations of arsenious anhydride and antimonious oxide have long been known, and the corresponding tribasic phosphates and arseniates offer some of the most striking exemplifications of isomorphism. Chlorine unites with the members of this group in the proportion of 3 atoms to 1 atom of phosphorus, arsenicum, or antimony. Bismuth is also related to this group by the composition and character of its oxides and chloride; although no bismuthated hydrogen is at present known. Nitrogen, as already pointed out, is connected with the phosphorus group by its combination with hydrogen ( $H_3N$ ), and by its formation of anhydrides with 3 and with 5 atoms of oxygen. An interesting isomorphous relation exists between the members of the sulphur and those of the phosphorus group; sulphur being isomorphous with arsenicum, as is shown in the correspondence in form between crystals of iron pyrites ( $FeS_2$ ), and those of mispickel ( $FeSAs$ ).

The following table exhibits some of the corresponding compounds of the 5 triads just mentioned:—

Ammonia.	Phosphuretted hydrogen.	Arsenuretted hydrogen.	Antimoniuretted hydrogen.	
$H_3N$	$H_3P$	$H_3As$	$H_3Sb$	
Nitrous chloride.	Phosphorous chloride.	Arsenious chloride.	Antimonious chloride.	Bismuth chloride.
$Cl_3N$	$Cl_3P$	$Cl_3As$	$Cl_3Sb$	$Cl_3Bi$
	Phosphoric chloride.		Antimonic chloride.	
	$Cl_5P$		$Cl_5Sb$	
Nitrous anhydride.	Phosphorous anhydride.	Arsenious anhydride.	Antimonious oxide.	Bismuth sesquioxide.
$N_2O_3$	$P_2O_3$	$As_2O_3$	$Sb_2O_3$	$Bi_2O_3$
Nitric anhydride.	Phosphoric anhydride.	Arsenic anhydride.	Antimonic anhydride.	Bismuthic anhydride.
$N_2O_5$	$P_2O_5$	$As_2O_5$	$Sb_2O_5$	$Bi_2O_5$

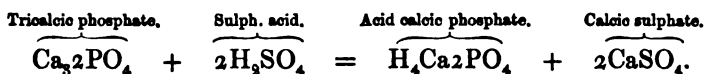
A gradation of properties is observed in these elements, and particularly in the three intermediate ones: phosphorus is the least dense, the most fusible and volatile; next follows arsenicum, and then antimony, in the order of their atomic weights. The

acid properties of the oxidized compounds are most marked in nitrogen, then in phosphorus; they are weaker in arsenicum, still weaker in antimony, and are scarcely apparent in bismuth. The compounds with hydrogen follow the same order: ammonia is a powerful base and requires a high temperature for its decomposition, phosphuretted hydrogen a very feeble base: in arseniuretted hydrogen the basic character is not perceived, although manifest in some of its derivatives, and the same thing is true of antimony; each of the three hydrides last mentioned being in succession more easily decomposed by simple exposure to heat, whilst the attraction of bismuth for hydrogen is so feeble that its hydride is unknown.

(443) PHOSPHORUS was discovered by Brandt in 1669. It is never met with in nature in the uncombined state, but it occurs in small proportion as tricalcic diphosphate ( $\text{Ca}_3\text{P}_2\text{O}_8$ ), as a constituent of the primitive and volcanic rocks, by the gradual disintegration of which it passes into the soil: from the soil it is extracted by plants, which accumulate it, particularly in their seeds, in quantity sufficient for the support of the various tribes of animals which they supply with food. In the animal system it is collected in large amount, and when combined with oxygen and calcium, as a particular form of calcic phosphate (*bone phosphate*,  $\text{Ca}_4\text{H}_3\text{P}_2\text{O}_{14}$ ), it forms the principal earthy constituent of the bones of the vertebrata. Phosphorus also appears to be essential to the exercise of the higher functions of the animal, since it exists as a never-failing ingredient in the substance of which the brain and nerves are composed. It is likewise contained in albumin and in fibrin in small proportions, and is present in the form of phosphates of the metals of the alkalies and of the earths in the urine and solid excrements of animals.

*Extraction.*—Phosphorus was originally extracted from the salts contained in urine, but it is now obtained almost exclusively from the bones of animals, or from native calcic phosphate. In order to prepare it, bones were formerly always burned to whiteness by calcining them in an open fire for some hours, and then reduced to powder; but now the gelatin of the bones is first economized by heating them, under pressure, with water; or the bones are distilled in closed vessels, the ammonia and volatile products are collected, whilst the bone black is employed in sugar-refining, and after it has become useless for this purpose, it is burned in the open fire. Three parts of bone-ash obtained by any of these methods are mixed with 2 of concentrated sul-

phuric acid, or 3 parts of crude acid of sp. gr. 1550, and 18 or 20 parts of water. The mixture is allowed to stand for two or three days, after which it is placed upon a strong linen filter, and the acid liquid is separated from the calcic sulphate by pressure; the residue is further washed with water, and the washings are added to the filtered solution. In this process the sulphuric acid is added in such quantity as partially to decompose the calcic phosphate; two-thirds of the calcium are removed by it in the insoluble form, as calcic sulphate, the remaining third being left as an acid salt, in combination with the whole of the phosphoric acid, with which it forms a compound readily soluble in water, frequently described as *superphosphate of lime* (calcic-tetrahydric diphosphate;  $\text{H}_4\text{Ca}_2\text{PO}_4$ ). The reaction may be thus expressed in symbols:—



This acid solution is evaporated to the consistence of a syrup, then mixed with from one-fourth to one-half its weight of charcoal, and heated to incipient redness in an iron pot, stirring constantly. The mass,

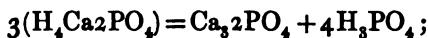
FIG. 319.

while hot, is transferred to an earthen retort (*a* fig. 319), which is covered externally with a thin paste, consisting of a mixture of equal parts of borax and fire-clay, with a view of rendering the retort less porous. It is then exposed to a heat which is slowly raised to a full red. Phosphorus gradually rises in vapour, and is conveyed by means of a wide copper tube,

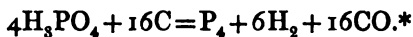


bent as at *b*, so as to dip into water contained in a vessel provided with a smaller tube, open at both ends, for conveying the uncondensed gases into a chimney. The phosphorus is condensed in yellow drops. In this operation it is found necessary to convert the normal phosphate into superphosphate of calcium; since the bone-ash, when heated with charcoal, does not part with its phosphorus. The superphosphate, when heated with charcoal, is decomposed; the calcium retains sufficient

phosphion to reconstitute the tribasic phosphate, which remains unchanged in the retort, while the excess of acid and the water which the mass always contains are decomposed by the charcoal; hydrogen, carbonic oxide, and phosphorus are the results. Gaseous matters escape, therefore, during the whole operation, which may be regarded as consisting of two stages, the first being the decomposition of the superphosphate into tribasic calcic phosphate and phosphoric acid:—



whilst the second stage consists of the deoxidation of the liberated acid:—



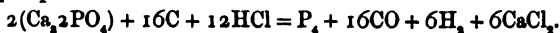
With a view to render the phosphorus perfectly pure, it is fused under warm water, with a solution of bleaching powder, and squeezed through wash-leather; or it may be fused, first under ammonia, and then under a solution of potassic dichromate in diluted sulphuric acid. The easy fusibility of phosphorus enables it to be moulded into sticks with facility; it is melted under water and forced into tubes, in which it is allowed to solidify.

*Properties.*—Phosphorus is a soft, semi-transparent, colourless, waxy-looking solid, which, however, becomes hard and brittle at low temperatures: it fumes in the air, emitting white vapours of an alliaceous odour. It has a specific gravity of 1.83 at 50° (10° C.) (Schrötter). It fuses at 111°·5 (44°·2 C.), and if melted under an alkaline liquid and allowed to cool undisturbed, it will long continue fluid at ordinary temperatures, but when touched with a wire or a glass rod it solidifies suddenly. Phosphorus is a non-conductor of electricity, both in the solid and the liquid state. It is extremely inflammable, taking fire in the open air at a temperature very little above its fusing-point. If it contain impurities, such as oxide of phosphorus, it takes fire still more easily. Great caution is therefore required in handling it; it is better always to cut it under water. The burns occasioned by melted phosphorus are deep and often extremely severe, from the difficulty of extinguishing the flame.

Phosphorus burns with a brilliant white flame, and emits

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\* Phosphorus may also be obtained by heating an intimate mixture of charcoal and tricalcic phosphate or of bone-ash to bright redness in a current of hydrochloric acid gas, carbonic oxide and hydrogen being liberated along with vapour of phosphorus while calcic chloride is formed:—



dense white fumes of phosphoric anhydride. In closed vessels it boils at about  $550^{\circ}$  ( $288^{\circ}$  C.), giving off a colourless vapour, of which 100 cubic inches calculated at 30 inches Bar. and  $60^{\circ}$ , would weigh about 135 grains. An atom of phosphorus, therefore, gives off a volume of vapour equal to only half that of an atom of oxygen; and, according to Deville, no alteration in the relative volumes of the two is effected by a temperature of  $1904^{\circ}$  ( $1040^{\circ}$  C.). Phosphorus is insoluble in water; it is slightly soluble in ether, but more so in benzol, in oil of turpentine, and in the fixed and essential oils. It is also freely dissolved by chloride of sulphur, by phosphorous chloride, and by carbonic disulphide: when its solution in the disulphide is allowed to fall upon filtering-paper in the open air, the finely divided phosphorus absorbs oxygen so rapidly that it takes fire as soon as the solvent has evaporated. If the solution be allowed to evaporate slowly in a current of hydrogen or carbonic anhydride, the phosphorus may be obtained crystallized in rhombic dodecahedra.

The vapour of phosphorus when suspended in hydrogen gives to the gas the property of burning with a green flame, in which are seen, when viewed by the prism, two intense green lines, one of which appears to coincide with one of the lines of barium: common amorphous phosphorus, hypophosphites, and phosphites, when introduced into Marsh's apparatus, give rise to this phenomenon, which is sufficiently sensitive to serve as a qualitative test of the presence of phosphorus.

Phosphorus is always preserved under water, for when exposed to the air, at all temperatures above  $32^{\circ}$  ( $0^{\circ}$  C.) it gradually combines with oxygen, and undergoes a slow combustion; under these circumstances, in a darkened room it emits a pale greenish light (hence its name, from  $\phi\omega\varsigma$ , light,  $\phi\omicron\rho\omicron\varsigma$ , bearing) attended with the production of the white fumes and the garlic odour already mentioned. The luminosity of phosphorus is prevented by the admixture of certain inflammable vapours and gases in minute quantity with the atmosphere; if air be mixed with either  $\frac{1}{150}$  of its bulk of olefant gas,  $\frac{1}{1150}$  of naphtha vapour, or  $\frac{1}{111}$  of vapour of oil of turpentine, a stick of phosphorus no longer appears luminous when exposed to its action (Graham).

It is remarkable that in pure oxygen the luminosity is not observed until the temperature rises to  $59^{\circ}$  ( $15^{\circ}$  C.), unless the gas be rarefied, or be diluted with some other gas.

(444) *Different forms of Phosphorus.*—Phosphorus assumes several different forms under the influence of causes apparently trifling. The *transparent* variety has been already mentioned;



this, when kept exposed to light under water, assumes a second form, consisting of small plates; it then appears to be *white* and opaque, and is somewhat less fusible. It has a sp. gr. of 1.515: white phosphorus becomes reconverted into the vitreous variety by a temperature not exceeding  $122^{\circ}$  ( $50^{\circ}$  C.). A third form is obtained by suddenly cooling melted phosphorus; it is perfectly *black* and opaque, but by simple fusion and slow cooling it again becomes transparent and colourless; whilst a fourth or *viscous* modification, analogous to viscous sulphur, may be obtained by heating very pure phosphorus to near its boiling-point and suddenly cooling it. A fifth form occurs in the shape of *red scales*, which are obtained by the spontaneous sublimation of phosphorus in the Torricellian vacuum when exposed to the rays of the sun.

*Red or amorphous Phosphorus.*—The red form of phosphorus has been carefully studied by Schrötter (*Ann. de Chimie*, III. xxiv. 406). It may be obtained by placing a quantity of dried common phosphorus in a flask from which the air is displaced by means of a current of carbonic anhydride; to the neck of the flask a long narrow tube, bent downward, is attached; the open end of this tube dips into a little mercury. Heat is next applied to the flask by means of an oil-bath: the phosphorus melts readily, but by regulating the heat steadily between  $446^{\circ}$  and  $464^{\circ}$  ( $230^{\circ}$  and  $240^{\circ}$  C.) by means of a thermometer plunged into the oil-bath, and maintaining it for 30 or 40 hours, almost all the phosphorus will become converted into the solid amorphous variety. When the change appears to be complete, the apparatus is allowed to cool: carbonic disulphide is then poured upon the mass in the flask, and digested on it for some hours: this is poured off, and fresh disulphide added, the digestion being repeated so long as any phosphorus is dissolved; this may be known by allowing a few drops of the decanted liquid to evaporate spontaneously in a watch-glass; any dissolved phosphorus will be left behind.

The red powder of which the undissolved portion consists, if not quite free from unaltered phosphorus, takes fire spontaneously when exposed to the air; if quite pure, it does not take fire; but it absorbs oxygen very slowly, the oxidation being more rapid if the powder be moist; phosphorous acid is gradually formed, and from its deliquescent character the powder becomes damp. This oxidation occurs so slowly that it was at first imagined that amorphous phosphorus underwent no change by exposure to the air. The higher the temperature at which the transformation is effected, the deeper is the colour of the product, which in the finest specimens rivals that of vermilion. By heating the phosphorus

more strongly during its preparation, the change may be produced much more rapidly, but the phosphorus then assumes the form of reddish-brown friable masses, with a conchoidal fracture. This form of phosphorus is manufactured at Birmingham on a considerable scale. The process occupies some weeks, and is not unattended with danger; for if the red powder be heated up to the point at which its re-conversion into the transparent variety takes place, the whole mass suddenly passes back into the ordinary form, with a copious evolution of heat, followed by the sudden formation of a large volume of the vapour of phosphorus. The purification from ordinary phosphorus may be effected by grinding the mass to a fine powder under water and boiling it with a solution of caustic soda so long as phosphuretted hydrogen is formed. The residual red phosphorus is then thoroughly washed from sodic hypophosphite, and afterwards dried. The changes produced in phosphorus by heat may be readily watched by placing a few fragments of well-dried phosphorus in a tube, upon which two or three bulbs have been blown, then expelling the air by a current of carbonic anhydride, and sealing one end of the tube,—the open end being made to dip into mercury. On applying heat to the phosphorus it becomes red, but on continuing to raise the temperature it distils over in perfectly colourless transparent drops, which frequently remain liquid for some hours, though they ultimately solidify to a transparent colourless mass.

Red or amorphous phosphorus differs remarkably in many of its properties from the waxy-looking stick phosphorus. It may be exposed to the air without emitting any odour. It is not soluble in either carbonic disulphide, phosphorous chloride, or benzol. The density of amorphous phosphorus exceeds that of the vitreous form; the red powder, according to Brodie, having a specific gravity of 2.14. It may be heated in the open air without change till the temperature reaches  $500^{\circ}$  ( $260^{\circ}$  C.); at this point it melts and bursts into flame, and burns with the dazzling brilliancy of common phosphorus, emitting dense fumes of phosphoric anhydride. Chlorine acts directly upon red phosphorus without the application of heat: the temperature rises, but the phosphorus does not take fire. When rubbed with potassic chlorate it detonates, very slight friction being sufficient to produce the action: peroxide of manganese and peroxide of lead act with it in a similar way, but less readily.

The principal consumption of phosphorus is in the manufacture of lucifer matches. In the usual mode of preparing these matches, the ends of the pieces of wood are first dipped in melted paraffin, or are gummed, and dusted over with sulphur, and then tipped with a mixture, in which the chief ingredients are an

emulsion of phosphorus in glue, and potassic chlorate, or black oxide of manganese. The manufacture is one attended with danger, from the highly inflammable and explosive nature of the ingredients used; but, in addition to this risk, those employed in the business are liable to a distressing form of caries of the lower jaw, arising from the action of the fumes of phosphorus upon those who inhale them. Of these evils, the first is greatly lessened, and the second altogether avoided, by the use of amorphous phosphorus. An ingenious plan for diminishing the risk of fires from the use of lucifer matches consists in separating the phosphorus from the other combustible ingredients; a mixture of amorphous phosphorus with half its weight of powdered glass is attached by means of size to the rubbing surface for kindling the matches; the composition with which they are tipped (a mixture of potassic chlorate, antimonious sulphide, and powdered glass), takes fire when rubbed upon the phosphorized surface, but not by ordinary friction upon any other substance, as the match itself contains no phosphorus.

Although vitreous phosphorus acts as a powerful irritant poison upon animals when taken internally, the amorphous variety may be swallowed with impunity; the vitreous phosphorus forms the active ingredient in the phosphorus paste frequently used to destroy cockroaches and other kinds of vermin.

Owing to its strong attraction for oxygen, phosphorus reduces some of the soluble compounds of the metals to the metallic state; a stick of phosphorus placed in a solution of auric chloride or of argentic nitrate becomes speedily incased in reduced gold or silver. Salts of palladium, platinum, and copper, are also reduced gradually when a stick of phosphorus is immersed in their solutions.

(445) OXIDES OF PHOSPHORUS.—Phosphorus is usually stated to furnish four compounds with oxygen, but only two of them are known in the anhydrous condition, viz. :—

			In 100 parts.	
			Phosphorus.	Oxygen.
Phosphorous anhydride ... ..	$P_2O_3 = 110$		56.36	43.64
Phosphoric anhydride ... ..	$P_2O_5 = 142$		43.66	56.34

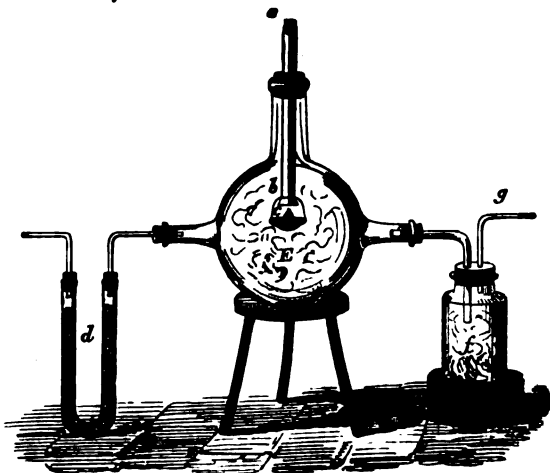
Phosphorus forms three oxidized acids, which are respectively monobasic, dibasic, and tribasic, in proportion as the quantity of oxygen increases: these acids are the following :—

Hypophosphorous acid (monobasic)  $HPH_2O_2$   
 Phosphorous acid (dibasic) . . .  $H_2PHO_3$   
 Phosphoric acid (tribasic) . . .  $H_3PO_4$

(446) PHOSPHORIC ANHYDRIDE:  $P_2O_5 = 142$ .—The most important of the oxides of phosphorus is that which when acted on by water forms phosphoric acid; it occurs native in considerable quantity in the form of tricalcic diphosphate ( $Ca_3P_2O_8$ ). The anhydride of this acid is the sole product of the rapid combustion of phosphorus in dry oxygen or in atmospheric air. By means of

the apparatus shown in fig. 320, a large quantity of phosphoric anhydride may be readily obtained in a few hours: *E* is a three-necked globe, in the centre of

FIG. 320.



which is suspended a porcelain dish, *c*; this dish is attached by means of platinum wire to the wide tube *a b*, which is closed at *a* with a cork; the bottle, *f*, is connected by the tube *g*, with an aspirator, or other convenient means of maintaining a continuous current of air through the apparatus: the air as it enters is thoroughly dried by passing over pumice moistened with sulphuric acid, in the tube, *d*. A fragment of well dried phosphorus is placed in the dish, *c*, and kindled by touching it with a hot wire. As the phosphorus burns away fresh pieces are added through the aperture *a*, which is again immediately closed with the cork. The anhydride thus obtained generally contains traces of one of the lower oxides of phosphorus. It forms a snow-white, flocculent, non-crystalline, anhydrous, but extremely deliquescent, powder, which fuses at an elevated temperature, and by a still stronger heat, approaching to whiteness, may be sublimed. When dropped into water it combines with it, emitting a hissing noise; the greater part is instantly dissolved, leaving a few gelatinous flocculi, which slowly disappear;  $\text{P}_2\text{O}_5 + 3\text{H}_2\text{O} = 2\text{H}_3\text{PO}_4$ . After it has once been dissolved, it cannot again be converted into the anhydride by mere elevation of temperature, as the whole compound is gradually dissipated in vapour. It does not emit vapour at ordinary temperatures: owing to its powerful attraction for water, this anhydride is often used as a desiccating and dehydrating agent; and for this purpose it surpasses in efficacy almost every known substance.

(447) *Hydrates of Phosphoric Acid*.—The pure acid is generally procured in a hydrated state, by boiling 1 part of phosphorus in 13 parts of nitric acid of sp. gr. 1.20. The phosphorus becomes

oxidized by the nitric acid, which is decomposed with escape of nitric oxide, and the phosphoric acid is dissolved as it is formed. When the phosphorus has all disappeared, the excess of nitric acid is expelled by evaporating the liquid in a platinum vessel until dense white fumes begin to arise; on cooling, the acid solidifies to a transparent glassy mass, frequently termed *glacial phosphoric acid*. This glacial acid is extremely deliquescent, producing a solution which, when saturated, has a sp. gr. of 2.0. It is intensely acid, but not caustic.

The oxidation of phosphorus by nitric acid furnishes an easy means of ascertaining the composition of phosphoric anhydride. For this purpose 3.1 grms. of phosphorus are boiled in a glass retort with pure diluted nitric acid. The greater part of the excess of water and nitric acid having been distilled off, the acid solution is added to 35 grms. of oxide of lead, in a weighed platinum dish: the liquid is slowly evaporated, and the residue ignited; by a red heat the whole of the nitric acid is expelled, and the phosphoric anhydride alone remains in combination with the oxide of lead. The oxide and anhydride together will be found to weigh 42.1 grms., showing an increase in weight upon the phosphorus and oxide of lead of 4.0 grms.: 31 parts of phosphorus therefore require 40 parts of oxygen for conversion into phosphoric anhydride.

A less pure acid is procured by adding to a solution of superphosphate of lime (prepared from bones by the process already described as a preliminary step towards procuring phosphorus) ammoniacal sesquicarbonate till effervescence ceases; tricalcic diphosphate is precipitated, leaving triammonic phosphate in solution. The precipitated calcic phosphate is separated by filtration, the liquid evaporated to dryness, and the residue ignited. Ammonia is expelled, and phosphoric acid (contaminated with all the soluble salts which the bones contained) remains behind.

There are three different forms of phosphoric acid, each of which possesses the properties of a distinct acid: viz.—

Metaphosphoric acid . . . . .	$\text{HPO}_3$
Orthophosphoric or ordinary phosphoric acid	$\text{H}_3\text{PO}_4$
Pyrophosphoric acid . . . . .	$\text{H}_4\text{P}_2\text{O}_7$

These different forms of the acid retain their peculiar characteristics when dissolved in water, and form salts with 1, with 3, or with 4 equivalents of basyls, according as the metaphosphoric, the orthophosphoric, or the pyrophosphoric acid is employed. Owing to the important influence which the study of these com-

binations has exercised upon the theory of saline combinations in general, it will be necessary to examine them somewhat in detail.

(448) *Orthophosphoric* (from  $\acute{o}\rho\theta\acute{o}\varsigma$ , right) or *Tribasic Phosphoric Acid*, *Trihydric Phosphate* ( $H_3PO_4$ ).—If the liquid formed by dissolving the glacial acid in water be boiled for some time, and sodic carbonate be then added until the solution becomes slightly alkaline, a tribasic hydro-disodic phosphate is obtained, which on evaporation crystallizes in large transparent rhombic prisms ( $Na_2HPO_4 \cdot 12H_2O$ ). If this solution be mixed with a neutral solution of argentic nitrate, a canary-yellow precipitate of triargentic phosphate ( $Ag_3PO_4$ ) is formed. Although this solution was neutral or slightly alkaline before admixture with argentic nitrate, it will be found afterwards to have a decidedly acid reaction upon litmus, nitric acid having been liberated :—



Plumbic acetate ( $Pb_2C_2H_3O_2$ ) may be used as a precipitant instead of argentic nitrate, and in this case a white triplumbic diphosphate ( $Pb_3_2PO_4$ ) subsides. If this phosphate of lead be well washed, suspended in water, and exposed to the action of a current of sulphuretted hydrogen, pure orthophosphoric acid is liberated and becomes dissolved in the liquid, whilst the black insoluble plumbic sulphide is formed;  $Pb_3_2PO_4 + 3H_2S = 2H_3PO_4 + 3PbS$ . The plumbic sulphide may be removed by filtration, and the acid obtained in deliquescent hard, brittle, prismatic, transparent crystals, by evaporation *in vacuo* over sulphuric acid. The orthophosphoric is a tribasic acid; and therefore it requires 3 atoms of a monad basyl for saturation. The salts of this hydrate form the *orthophosphates* or common *tribasic phosphates*.

There are three varieties of these salts, which may be indicated by general formulæ as follows :—

- |                                |            |
|--------------------------------|------------|
| 1 Basic phosphates . . . . .   | $M_3PO_4$  |
| 2 Neutral phosphates . . . . . | $M_2HPO_4$ |
| 3 Acid phosphates . . . . .    | $MH_2PO_4$ |

It is not necessary that the 3 equivalents of basyl should consist of the same metal in these salts: two or even three different basyls may coexist in the salt; as, for example, in microcosmic salt, or sodio-ammonio-hydric phosphate ( $NaH_4NHPO_4 \cdot 4H_2O$ ).

In the first class, the 3 atoms of hydrogen in the acid have been displaced by 3 equivalents of a metal, as, for example, in the trisodic phosphate ( $Na_3PO_4 \cdot 12H_2O$ ); these salts when soluble have a strongly alkaline reaction: in the second class, 2 atoms of the basic hydrogen have been displaced by 2 equivalents of a

metal; they are like the ordinary rhombic hydro-disodic phosphate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ); the soluble salts of this class are neutral, or have a feebly alkaline reaction: whilst the third class contains only 1 equivalent of metal with 2 atoms of basic hydrogen; they are of the form of the sodio-dihydric phosphate ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ), formerly called the biphosphate of soda; these salts have a strongly acid reaction, and are often spoken of as the *super-phosphates*.

*Tests.*—The soluble orthophosphates are characterized by the yellow triargentic phosphate which their neutral solutions form with argentic nitrate; this precipitate is freely soluble both in nitric acid and in ammonia. They also yield a crystalline precipitate when a clear solution of magnesian sulphate, rendered alkaline by ammonia, is briskly stirred with them; this precipitate is insoluble in water which contains free ammonia; it consists of ( $\text{Mg}'\text{H}_4\text{NPO}_4 \cdot 6\text{H}_2\text{O}$ ): when ignited, the water and ammonia are expelled, and it becomes converted into dimagnesian pyrophosphate ( $\text{Mg}_2\text{P}_2\text{O}_7$ ), a compound frequently employed as a means of estimating the amount of phosphates in solutions which contain them: 100 parts of the ignited residue corresponding to 63.96 of  $\text{P}_2\text{O}_5$ .\* Neutral solutions of the orthophosphates give precipitates with salts of barium and calcium; the tribasic and tricalcic diphosphates are readily soluble in acetic acid; but free phosphoric acid gives no precipitate in solutions of the nitrates of calcium, barium, or silver, or in solution of ferric chloride; when ammoniac molybdate is added to a solution of a phosphate acidulated with nitric acid, a characteristic yellow precipitate of ammoniac molybdophosphate is formed; the deposition of this precipitate is favoured by boiling the liquid.

The quantity of phosphoric acid in a solution may be ascertained, if neither sulphuric nor hydrochloric acid be present, by means of plumbic acetate; the solution, before this salt is added to it, should be neutralized by ammonia, and then acidulated freely with acetic acid; the precipitate ( $\text{PbHPO}_4$ ) should be well washed and ignited, by which means it is rendered anhydrous; 100 parts of the ignited residue represent 24.14 of ( $\text{P}_2\text{O}_5$ ). Chancel has lately shown that the acid solution of bismuth trinitrate ( $\text{Bi}'''_3\text{NO}_3$ ) furnishes an admirable method of separating phosphoric acid from many metals, such as iron, calcium, and aluminum, which form phosphates soluble only in acidulated liquids. Care is requisite to remove any chlorine or sulphuric acid from the liquid, before adding the solution of bismuth, which is prepared by dissolving 1 part of the crystallized nitrate in 4 parts of nitric acid of sp. gr. 1.36, adding 30 parts of water, then boiling, and filtering if necessary. In separating the bismuth phosphate by this reagent, the liquid must be boiled, and the precipitate well washed with

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\* The arseniates give precipitates both with ammoniacal salts of magnesium and molybdic acid, similar to those furnished by the phosphates.

boiling water and carefully dried : 100 parts of bismuth phosphate ( $\text{BiPO}_4$ ) correspond to 23.28 of phosphoric anhydride ( $\text{P}_2\text{O}_5$ ). With ferric salts phosphoric acid forms an insoluble buff-coloured precipitate of ferric orthophosphate ( $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ), which is also sometimes employed to estimate the quantity of phosphoric acid in a solution.

(449) *Pyrophosphoric Acid; Tetrahydric Pyrophosphate* ( $\text{H}_4\text{P}_2\text{O}_7$ ).

—When hydro-disodic (rhombic) phosphate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ) is exposed to heat, it melts in its water of crystallization ; and by continuing to apply to it a temperature not exceeding  $302^\circ$  ( $150^\circ \text{C.}$ ), it may be reduced to a hard, white, saline mass, which may be redissolved in water with all its former properties. The dry mass consists of  $\text{Na}_2\text{HPO}_4$ . If, however, it be heated to redness before redissolving, 2 atoms of the salt coalesce and a new salt is formed ; 1 atom of water is expelled ;  $2\text{Na}_2\text{HPO}_4$  becoming  $\text{Na}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$  ; on redissolving the residue in water and evaporating the solution, the liquid no longer furnishes rhombic but acicular crystals, composed of  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  ; and the solution, instead of yielding a yellow precipitate with argentic nitrate, now gives a white one, consisting of  $\text{Ag}_4\text{P}_2\text{O}_7$ . In this case, the solution, if neutral to litmus before intermixture with the silver salt, remains neutral afterwards, because no free acid is liberated ;  $4\text{AgNO}_3 + \text{Na}_4\text{P}_2\text{O}_7 = 4\text{NaNO}_3 + \text{Ag}_4\text{P}_2\text{O}_7$ .

With a solution of plumbic acetate, sodic pyrophosphate also occasions a white precipitate, the composition of which is represented by the formula  $\text{Pb}_2\text{P}_2\text{O}_7$  ; and if the lead salt be suspended in water, and decomposed with sulphuretted hydrogen, it yields a solution of pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ ). The excess of sulphuretted hydrogen must be got rid of by exposure to the air (not by heat, otherwise the tribasic acid is formed by the assimilation of water ;  $\text{H}_2\text{O} + \text{H}_4\text{P}_2\text{O}_7 = 2\text{H}_3\text{PO}_4$ ), and the acid may be obtained in crystals by evaporation *in vacuo* over sulphuric acid. This tetra-sodic phosphate, from the mode in which it is obtained, is usually termed (from  $\pi\upsilon\rho$ , fire) the *pyrophosphate* of sodium, and the corresponding salts of the acid, *pyrophosphates*. No solid pyrophosphate of potassium or of ammonium can be obtained ; these salts are stable while in solution, but on evaporation they become converted into tribasic phosphates by the assimilation of water (Graham). The pyrophosphoric appears to be a tetra-basic acid : two classes of pyrophosphates may be procured ; one with 4 atoms of a fixed basyl, with the formula  $\text{M}_4\text{P}_2\text{O}_7$ , like the ordinary sodic pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) ; the other containing 2 atoms of hydrogen and 2 of a uniequivalent metal ( $\text{M}_2\text{H}_2\text{P}_2\text{O}_7$ ), corresponding in composition to the acid pyrophosphate of sodium, or disodio-dihydric pyrophosphate ( $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ).



Neutral solutions of the pyrophosphates also give in solutions of salts of calcium and barium white precipitates, which are the pyrophosphates of these metals; salts of nickel and copper when mixed with a solution of sodic pyrophosphate yield double salts, containing 2 atoms of sodium to 3 of the other metal;  $2\text{Na}_4\text{P}_2\text{O}_7 + 3\text{Cu}''2\text{NO}_3 = \text{Cu}''_3\text{Na}_22\text{P}_2\text{O}_7 + 6\text{NaNO}_3$ .

(450) *Metaphosphoric Acid; Hydric Metaphosphate* ( $\text{HPO}_3$ ).—If, in preparing the rhombic, or hydro-disodic phosphate (448), two equal portions of phosphoric acid be taken, and after neutralizing one portion with sodic carbonate, as above directed, the second quantity of acid be added to the neutralized solution, a tribasic sodio-dihydric phosphate, consisting of  $\text{NaH}_2\text{PO}_4$ , will be obtained on evaporating the liquid to dryness; but on igniting the residue, the 2 atoms of hydrogen will be expelled in the form of water, and a fusible monobasic phosphate of sodium, or *sodic metaphosphate* ( $\text{NaPO}_3$ ), will remain in the form of a transparent glass. This, if dissolved in water, gives with argentic nitrate a gelatinous white precipitate ( $\text{AgPO}_3$ ) different in appearance and composition from either of the former phosphates of silver; it is soluble in excess of the sodium salt. With plumbic acetate a white precipitate also is formed ( $\text{Pb}_2\text{PO}_3$ ): it is fusible in boiling water, and when decomposed with sulphuretted hydrogen it yields the corresponding acid ( $\text{HPO}_3$ ), which is distinguished from the other hydrates by its power of coagulating the albumin of white of egg. It also gives white precipitates with baric chloride and argentic nitrate. Acetic acid does not coagulate albumin, neither does a solution of sodic metaphosphate; but if the two solutions be mixed, the acetic acid liberates metaphosphoric acid, and the albumin becomes coagulated. Tribasic phosphoric acid by prolonged heating to redness loses water, the glassy residue being converted almost entirely into metaphosphoric acid. Sodic metaphosphate is capable of combining with water of crystallization, which it retains if dried at  $212^\circ$  ( $100^\circ\text{C.}$ ): this water is not basic, for on again dissolving the salt it gives the usual reactions of the metaphosphates. If, however, the salt be heated to  $302^\circ$  ( $150^\circ\text{C.}$ ), it does not lose weight, but becomes converted into the disodio-dihydric pyrophosphate, the water by the application of heat having changed its function in the salt, its hydrogen having now become basic (Graham):—



This change of properties in the salt, without any change in the

proportions of its components, here admits of a satisfactory explanation; and it is a striking and instructive illustration of the facility with which chemical compounds, by a change in molecular constitution, may sometimes give rise to substances the properties of which may be very different, though the results of their analysis in 100 parts may numerically coincide.

Sodic metaphosphate forms with salts of barium a white insoluble baric metaphosphate ( $\text{Ba}_2\text{PO}_3$ ); but this precipitate when boiled becomes gradually dissolved, assimilating 2 atoms of water, and becoming converted into the tribasic baric-tetrahydric diphosphate ( $\text{BaH}_2\text{PO}_4$ ). The metaphosphoric is a monobasic acid. Solutions of the metaphosphates redden litmus feebly.

The aqueous solution of metaphosphoric acid, when boiled, becomes converted into the ordinary tribasic acid, consequently it cannot be concentrated by the action of heat,  $\text{HPO}_3 + \text{H}_2\text{O}$  becoming  $\text{H}_3\text{PO}_4$ : but the solution may be preserved at common temperatures without change.

The following table furnishes a synoptic view of some of the principal phosphates, metaphosphates, and pyrophosphates:—

#### I. ORTHOPHOSPHATES. $\text{M}_3\text{PO}_4$ ; $\text{M}_2\text{HPO}_4$ ; $\text{MH}_2\text{PO}_4$ .

Trisodic phosphate	...	...	...	...	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$
Hydrodisodic (rhombic) phosphate	...	...	...	...	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$
Sodio-dihydric (acid) phosphate	...	...	...	...	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
Microcosmic salt	...	...	...	...	$\text{NaH}_2\text{NHPO}_4 \cdot 4\text{H}_2\text{O}$
Calcic phosphate (native)	...	...	...	...	$\text{Ca}_3\text{P}_2\text{O}_7$
Superphosphate of calcium	...	...	...	...	$\text{Ca}''\text{H}_2\text{P}_2\text{O}_7$
Ammonio-magnesian phosphate	...	...	...	...	$\text{Mg}''\text{H}_2\text{N}_2\text{P}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$
Ferric phosphate	...	...	...	...	$\text{Fe}'''\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$
Triplumbic phosphate	...	...	...	...	$\text{Pb}''_3\text{P}_2\text{O}_7$
Bismuthic	...	...	...	...	$\text{Bi}'''\text{P}_2\text{O}_7$
Triargentic	...	...	...	...	$\text{Ag}_3\text{PO}_4$
Triargentic	...	...	...	...	$\text{Ag}_3\text{PO}_4$

#### II. METAPHOSPHATES. $\text{MPO}_3$ .

Sodic metaphosphate	...	...	...	...	$\text{NaPO}_3$
Plumbic	...	...	...	...	$\text{Pb}''_2\text{PO}_3$
Argentio	...	...	...	...	$\text{AgPO}_3$

#### III. PYROPHOSPHATES. $\text{M}_4\text{P}_2\text{O}_7$ ; $\text{MM}'_3\text{P}_2\text{O}_7$ .

Sodic pyrophosphate	...	...	...	...	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$
Plumbic	...	...	...	...	$\text{Pb}''_2\text{P}_2\text{O}_7$
Pyrophosphate of copper and sodium	...	...	...	...	$\text{Cu}''_2\text{Na}_2\text{P}_2\text{O}_7$
Argentio pyrophosphate	...	...	...	...	$\text{Ag}_4\text{P}_2\text{O}_7$

Fleitmann and Henneberg (*Liebig's Ann.* lrv. 324) have described two classes of salts which are probably anhydro-phosphates. By melting sodic pyrophosphate and sodic metaphosphate together, in the proportion of 1 atom of the pyrophosphate and 2 atoms of the metaphosphate, they obtained a salt,  $\alpha$ , consisting of  $2\text{Na}_4\text{P}_2\text{O}_7 \cdot \text{P}_2\text{O}_3$ ; and by fusing 8 atoms of the metaphosphate with 1 atom of the pyrophosphate, a definite sodium salt,  $\beta$ , was obtained, which con-

sisted of  $4\text{Na}_3\text{PO}_4, 3\text{P}_2\text{O}_5$ ; both these salts are very unstable, and in solution pass quickly into a mixture of pyrophosphate and metaphosphate. Definite salts of silver and of magnesium corresponding to these compounds were obtained.

Fleitmann and Henneberg propose to represent these various classes of salts as follows, comparing quantities of each which contain equal amounts of metallic basyl, the quantity of phosphoric anhydride successively increasing in each series :—

Orthophosphates	...	...	$6\text{M}_2\text{O}, 2\text{P}_2\text{O}_5$ or $4\text{M}_4\text{PO}_4$
Pyrophosphates	...	...	$6\text{M}_2\text{O}, 3\text{P}_2\text{O}_5$ $3\text{M}_4\text{P}_2\text{O}_7$
Fleitmann and Henneberg,	<i>a</i>		$6\text{M}_2\text{O}, 4\text{P}_2\text{O}_5$ $2\text{M}_4\text{P}_3\text{O}_{10}$
Ditto	ditto	<i>b</i>	$6\text{M}_2\text{O}, 5\text{P}_2\text{O}_5$ $\text{M}_{12}\text{P}_5\text{O}_{31}$
Metaphosphates	...	...	$6\text{M}_2\text{O}, 6\text{P}_2\text{O}_5$ $12\text{MPO}_3$

which case the pyrophosphates, as well as the salts discovered by Fleitmann and Henneberg, would be compounds of the orthophosphates with different proportions of a metaphosphate. A pyrophosphate, for example, may be represented thus;  $\text{Na}_2\text{PO}_4, \text{NaPO}_3 = \text{Na}_3\text{P}_2\text{O}_7$ ; the salt *a* being  $\text{Na}_2\text{PO}_4, 3\text{NaPO}_3 = \text{Na}_8\text{P}_4\text{O}_{18}$ , and the salt *b* being  $\text{Na}_2\text{PO}_4, 9\text{NaPO}_3 = \text{Na}_{20}\text{P}_5\text{O}_{31}$ .

*Modifications of Metaphosphoric Acid.*—If the ordinary or glassy sodic metaphosphate be fused and allowed to cool very slowly it furnishes a beautiful crystalline mass, and this, when dissolved in a small quantity of hot water, forms a liquid which divides into two strata; the smaller of these contains unchanged sodic metaphosphate; but the bulk of the liquid is a solution of the crystalline salt, which may be obtained on evaporation in oblique rhombic prisms ( $6\text{NaPO}_3, 12\text{H}_2\text{O}$ ): the solution of this salt is *neutral* and has a cooling saline taste, whilst that of the ordinary or vitreous metaphosphate is insipid. The crystalline salt, by boiling, is rapidly converted into the *acid* orthophosphate or sodic dihydric phosphate ( $\text{NaH}_2\text{PO}_4$ ); a beautifully crystallized silver salt, consisting of  $6\text{AgPO}_3, 2\text{H}_2\text{O}$ , may be obtained from the crystalline sodium salt by precipitation, and a similar lead salt ( $3\text{Pb}_2\text{PO}_3, 3\text{H}_2\text{O}$ ) may also be procured.

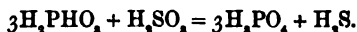
Maddrell (*Proceed. Chem. Soc.*, 1847, p. 273) has described a series of monobasic metaphosphates which are anhydrous, crystalline, and insoluble in water, but soluble in oil of vitriol. They were formed by heating a solution of the sulphate or nitrate of the metal with an excess of phosphoric acid, until the sulphuric or other acid of the salt was expelled. Salts of potassium, sodium, aluminum, copper, nickel, and others were thus procured. The sodium salt, if prepared with phosphoric acid which contains magnesium, or any metal isomorphous with magnesium, forms an insoluble double metaphosphate: the magnesium double salt is crystalline, and consists of  $(3\text{Mg}_2\text{PO}_3, 2\text{NaPO}_3)$ . These different varieties of metaphosphates are supposed to be due to the existence of several polymeric varieties of metaphosphoric acid, but the subject needs further investigation.

(451) PHOSPHOROUS ANHYDRIDE ( $\text{P}_2\text{O}_3$ ) may be procured by burning phosphorus in a limited current of dry air. A white, volatile, deliquescent, inflammable powder, destitute of crystalline structure, is thus obtained, often mixed with small quantities of oxide of phosphorus and phosphoric anhydride.

*Phosphorous acid; Dihydric phosphite* ( $\text{H}_2\text{PHO}_2$ ) may be obtained in solution by transmitting a stream of chlorine very slowly through a deep layer of phosphorus melted under water, so that each bubble of gas shall be completely absorbed by the phosphorus; phosphorous chloride ( $\text{PCl}_3$ ) is formed, and is immediately decomposed by the water into hydrochloric and phosphorous acids;  $\text{PCl}_3 + 3\text{H}_2\text{O} = \text{H}_2\text{PHO}_2 + 3\text{HCl}$ . If the acid liquid be concentrated by a heat

not exceeding  $392^{\circ}$  ( $200^{\circ}$  C.), hydrochloric acid is expelled, and the acid is obtained in deliquescent rectangular prisms. When exposed to the air it gradually absorbs oxygen; and by a high temperature it is decomposed into phosphoric acid and phosphuretted hydrogen ( $4\text{H}_2\text{PHO}_2 = 3\text{H}_2\text{PO}_4 + \text{H}_2\text{P}$ ). It is also furnished in a less pure form, by the slow combustion which occurs when phosphorus is left exposed to the action of the atmosphere; this may be safely effected by placing sticks of phosphorus separately in tubes open at both ends, the lower aperture of the tube being a little contracted so as to prevent the phosphorus from falling out; a number of these tubes are then placed in a funnel, and the dense acid liquid which is gradually formed drains into a vessel placed for its reception. In this process phosphorous acid is first produced; the acid being deliquescent attracts moisture from the air, and then, by gradually absorbing oxygen, it forms phosphoric acid. The oxidation never proceeds so far as to convert the whole into phosphoric acid; the liquid therefore contains a mixture of phosphorous and phosphoric acids, which was at one time supposed to be a peculiar oxide of phosphorus, and was termed *phosphatic acid*.

*Phosphites*.—Phosphorous acid is dibasic, and forms two classes of salts, the general formula of its normal salts being  $\text{M}_2\text{PHO}_2$ , while that of the acid phosphites is  $\text{M}'\text{HPHO}_2$ . Normal sodic phosphite, for instance, consists of  $\text{Na}_2\text{PHO}_2 \cdot 5\text{H}_2\text{O}$ ; when heated to  $300^{\circ}$  C., the 5 atoms of water are expelled. The acid phosphite of barium, dried at  $100^{\circ}$  C., consists of baric dihydro-diphosphite ( $\text{BaH}_2\text{PHO}_2$ ). The acid phosphites when heated emit hydrogen gas, whilst a metaphosphate remains behind; for example ( $\text{BaH}_2\text{PHO}_2$ ) becomes  $\text{Ba}_2\text{PO}_4 + 2\text{H}_2$ . The normal phosphites when heated emit both hydrogen and phosphuretted hydrogen; for instance, plumbic phosphite,  $5\text{PbPHO}_2 = \text{Pb}_2\text{PO}_4 + \text{Pb}_2\text{P}_2\text{O}_7 + \text{H}_2\text{P} + \text{H}_2$ . Free phosphorous acid does not immediately reduce potassic permanganate, unless heated with it; a reaction which distinguishes it from hypophosphorous acid, which, even in the cold, rapidly discharges the colour of the permanganate in acid solutions. The normal phosphites of the alkali-metals are freely soluble, most others but sparingly so; amongst them plumbic phosphite is the least soluble; it is also insoluble in acetic acid. With a solution of corrosive sublimate ( $\text{HgCl}_2$ ), acidulated with acetic acid, the phosphites give a white precipitate of calomel, the formation of which is hastened by heating the liquid. Another characteristic reaction is the reduction of sulphurous acid by a solution of the phosphites, with evolution of sulphuretted hydrogen, attended by simultaneous precipitation of sulphur, owing to the action of the sulphurous acid on the sulphuretted hydrogen:—



(452) **HYPOPHOSPHOROUS ACID**; *Hydric hypophosphite* ( $\text{HPH}_2\text{O}_2$ ).—This compound was formerly considered to be an acid of phosphorus with a still smaller quantity of oxygen than the preceding, but its anhydride has never been obtained. One of the hypophosphites is produced whenever phosphorus is boiled with a solution of caustic potash or soda, or with a hydrate of one of the alkaline earths. It may be procured in combination, by Rose's method of boiling phosphorus with hydrate of baryta in water; phosphuretted hydrogen escapes, and on evaporation a barium salt is obtained, composed of  $\text{Ba}_2\text{PH}_2\text{O}_2$ , owing to the following decomposition:  $3(\text{BaO}, \text{H}_2\text{O}) + 2\text{P}_4 + 6\text{H}_2\text{O} = 3(\text{Ba}_2\text{PH}_2\text{O}_2) + 2\text{H}_3\text{P}$ ; and on adding sulphuric acid cautiously, pure hypo-

phosphorous acid is obtained in solution, whilst the barium is separated as sulphate. Baric hypophosphite may also be prepared by heating phosphorus with a solution of baric sulphide, when free hydrogen with phosphuretted and sulphuretted hydrogen escape; the last traces of baric sulphide are removed by the addition of a little plumbic sulphate. Hypophosphorous acid forms an uncrystallizable syrup, which has a sour, bitterish taste; its acid properties are but feebly marked, and its solution gradually absorbs oxygen from the air. When heated, it first loses water; and by a stronger heat is decomposed, emitting phosphuretted hydrogen, whilst phosphoric acid is set free;  $2\text{HPH}_2\text{O}_3$  becoming  $\text{H}_3\text{PO}_4 + \text{H}_3\text{P}$ . Owing to the partial decomposition of the phosphuretted hydrogen, a little phosphorus is generally deposited at the same time, and a corresponding quantity of hydrogen is liberated.

*Hypophosphites.*—The researches of Dulong, of Rose, and of Wurtz have shown that the hypophosphites are monobasic, consequently the acid forms but a single class of salts, of which the normal formula is  $\text{M'PH}_2\text{O}_3$ . Sodid hypophosphite, for example, consists of  $\text{NaPH}_2\text{O}_3$ ; the lead salt may be represented as  $\text{Pb}_2\text{PH}_2\text{O}_3$ . They correspond, therefore, to the monobasic phosphates, but 2 atoms of hydrogen have taken the place of 1 atom of oxygen in the radicle of the acid. The hypophosphites are all soluble in water; many of them crystallize easily, by spontaneous evaporation; the crystallized salts may be preserved unchanged, but their solutions, when evaporated at a high temperature, are gradually converted into phosphites by absorption of oxygen. Like phosphorous acid they reduce gold and silver from their salts. The hypophosphites of the alkali-metals contain no water of crystallization: they are deliquescent, and also soluble in alcohol.\* Calcic hypophosphite ( $\text{Ca}_2\text{PH}_2\text{O}_3$ ) requires about 6 parts of cold water for solution, and is scarcely more soluble in boiling water. Each atom of the barium salt retains an atom of water when crystallized at ordinary temperatures, but if crystallized from a boiling solution is deposited in anhydrous tables ( $\text{Ba}_2\text{PH}_2\text{O}_3$ ). Magnesian hypophosphite ( $\text{Mg}_2\text{PH}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ ) crystallizes in brilliant, regular octohedra, which are efflorescent. The hypophosphites of nickel, cobalt, and iron, also retain  $6\text{H}_2\text{O}$ ; those of zinc and manganese retain but 1 atom of water of crystallization, which they lose at  $302^\circ$  ( $150^\circ \text{C.}$ ) Those of potassium, sodium, ammonium, and strontium, copper and lead, contain no water of crystallization.

Hypophosphorous acid is distinguished from phosphorous acid by a remarkable reaction with the salts of copper; if to an excess of free hypophosphorous acid a solution of cupric sulphate be added, and the liquid be warmed to about  $130^\circ$  ( $55^\circ \text{C.}$ ), a solid insoluble hydride of copper ( $\text{CuH}$ ) is precipitated. On raising the liquid which contains the precipitate, to the boiling-point, this hydride is decomposed into hydrogen gas and metallic copper.

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\* Sodid hypophosphite, which is now prepared largely for medicinal purposes, sometimes explodes spontaneously during the evaporation of its aqueous solution.

(453) OXIDE OF PHOSPHORUS ( $P_2O_3$ ).—A still lower degree of oxidation of phosphorus exists, which possesses neither acid nor alkaline properties. It is always formed in small quantity when phosphorus is burned in air, and is one of the constituents of the yellow or red residue after the combustion has terminated. It is not, however, a compound of any importance. Oxide of phosphorus has neither smell nor taste, and is quite insoluble in water.

(454) PHOSPHIDES OF HYDROGEN.—None of the compounds of phosphorus with hydrogen is possessed of acid characters: these compounds are three in number: viz.  $H_3P$ ,  $H_2P$ , and  $HP_2$ . The first is gaseous, the second liquid, and the third solid, at ordinary temperatures.

*Phosphuretted hydrogen gas: Phosphorous trihydride* ( $H_3P = 34$ ); *Rel. wt.* 17; *Theoretic Sp. Gr.* 1·175; *Observed*, 1·185; *Atomic and Mol. Vol.*  .—Phosphuretted hydrogen is a highly inflammable colourless gas, with a foetid alliaceous odour, liquefiable under pressure; it is slightly soluble in water; when transmitted through solutions of certain metallic salts such as those of lead, copper, or mercury, it is absorbed and decomposed; phosphides of the metals are produced and are precipitated. Those of lead and copper are black, that of mercury is yellow. Solutions of the salts of gold and silver are reduced to the metallic state, and phosphoric acid is found in solution. When the gas is pure it is wholly absorbed by a solution of chloride of lime. It is decomposed by sulphurous acid, as well as by chlorine, bromine, and iodine. A mixture of the gas with air or with oxygen explodes at a temperature of  $302^\circ$  ( $150^\circ$  C.), or sometimes even at common temperatures, if the pressure be suddenly diminished. In this gas half a volume of the vapour of phosphorus and 3 volumes of hydrogen are condensed into the space of 2 volumes. Its composition may therefore be thus represented:—

			By weight.		By vol.		Sp. gr.
Phosphorus ...	P	=	31	or 91·18	0·5	or 0·25	= 1·071
Hydrogen ...	$H_2$	=	3	8·82	3·0	1·5	= 0·104
<hr/>			<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Phosphuretted } hydrogen }	$H_3P$	=	34	100·00	2·0	1·0	= 1·175

The combining volume of phosphuretted hydrogen is the same as that of ammonia, to which it is analogous in composition; but it is without action upon either red or blue litmus. Some indication of a basic character is, however, shown by it, for it combines with certain of the acids in definite proportions. For example, its compound with hydriodic acid ( $H_3P, HI$ ) is formed by the union of equal volumes of the two gases, which in the act of combination do not undergo condensation, for its vapour, according

to Bineau, has a density of 2.77; it crystallizes in cubes, which fuse at a moderate heat, and if air be excluded it may be sublimed without alteration. These crystals are deliquescent, and are decomposed by water into hydriodic acid and phosphuretted hydrogen gas. This compound is easily prepared by introducing into a small retort 127 parts of dry iodine ground up with powdered glass, and 31 parts of phosphorus in small fragments, then adding 20 parts of water; the vapours which come off consist of the compound mixed with an excess of hydriodic acid; the hydriodate of phosphuretted hydrogen is condensed in crystals in the neck of the retort, if it be kept cool. A similar compound may be obtained with hydrobromic acid. Hofmann and Cahours have shown that by displacing the hydrogen in gaseous phosphide of hydrogen, by ethyl and other analogous hydrocarbons, compounds may be obtained which neutralize acids, and are powerfully basic.

Phosphuretted hydrogen combines with the perchlorides of many of the metals, such as those of tin, titanium, antimony, and iron. These compounds are decomposed by water, with escape of phosphuretted hydrogen gas.

*Preparation.*—Phosphuretted hydrogen gas may be obtained in a state of purity by the decomposition of phosphorous acid by heat;  $4\text{H}_2\text{PHO}_3$  yielding  $3\text{H}_3\text{PO}_4 + \text{H}_3\text{P}$ ; hypophosphorous acid gives an analogous result,  $2\text{HPH}_2\text{O}_2$ , becoming  $\text{H}_3\text{PO}_4 + \text{H}_3\text{P}$ .

Phosphuretted hydrogen, however, is generally prepared by heating fragments of phosphorus with a strong solution of caustic potash, or with cream of lime; hypophosphite of the metal is formed, with extrication of phosphuretted hydrogen;  $\text{P}_4 + 3\text{H}_2\text{O} + 3\text{KHO}$  becoming  $3\text{KPH}_2\text{O}_2 + \text{H}_3\text{P}$ . When potash is used, free hydrogen is also evolved, owing to the gradual decomposition of the hypophosphite when boiled with excess of free alkali, and the formation of phosphate. The gas so obtained has the remarkable property of taking fire spontaneously in atmospheric air or in oxygen gas; if allowed to escape into the air in bubbles, each bubble as it breaks produces a beautiful white wreath of phosphoric anhydride, composed of a number of ringlets revolving in vertical planes around the axis of the wreath itself, as it ascends; thus tracing before the eye, with admirable distinctness, the rapid gyratory movements communicated to the air contained in a bubble, when it is allowed to burst upon the surface of a still sheet of water. If the bubbles be allowed to rise into a jar of oxygen, a brilliant flash of light, attended with a slight concussion, accompanies the bursting of each bubble.

Owing to the spontaneous inflammation of the gas it should be made in small vessels containing but little atmospheric air. Graham has shown that the addition of small quantities of the vapour of some inflammable bodies, such as ether, naphtha, and oil of turpentine, destroys this self-lighting power; and that porous bodies, such as charcoal, also remove it. On the other hand, the gas obtained from phosphorous acid is not self-lighting, but the addition of so small a quantity as  $\frac{1}{10,000}$  of its bulk of the vapour of nitrous anhydride confers this property upon it.

(455) *Liquid Phosphide of hydrogen*:  $H_2P$ , or  $H_{10}P_4$ .—The singular property which phosphuretted hydrogen possesses, in certain cases, of igniting spontaneously when mixed with free oxygen long remained without explanation; as a careful analysis indicated little or no difference in composition between the self-lighting gas and the other variety, which does not possess this property. The true cause of the phenomenon was, however, traced a few years ago by P. Thénard, to the presence of a minute quantity of the vapour of another phosphide of hydrogen ( $H_{10}P_4$ ), which takes fire the instant that uncombined oxygen is presented to it (*Ann. de Chimie*, III. xiv. 5). This compound exists at ordinary temperatures as a volatile liquid, which by exposure to light is decomposed into a yellow, solid, and but slightly inflammable phosphide ( $HP_2$ ), and into the non-self-lighting gas ( $H_2P$ ); for  $H_{10}P_4 = HP_2 + 3H_2P$ . It had long been remarked, although analysis showed no difference between the self-lighting and the common gas, that when the former is exposed to the sunlight for a few hours, a solid yellow compound is deposited in small quantity upon the sides of the vessel, whilst the gas loses its self-lighting power; and that this power is also destroyed by exposing the gas to a great degree of cold. This effect is evidently due, in the case of the exposure to sunlight, to decomposition of the inflammable compound, and in the case of the application of cold, to its condensation into the liquid form.

Liquid phosphide of hydrogen may be prepared by conducting the gas which is disengaged by the action of water upon phosphide of calcium ( $CaP$ ), through a bent tube immersed in a freezing-mixture of ice and salt; a colourless liquid of high refracting power is thus condensed. It takes fire the instant that it comes into contact with air, and burns with the intense white light of phosphorus. Solar light quickly decomposes it into the solid phosphide ( $HP_2$ ) and into the gaseous phosphuretted hydrogen. If a little of the vapour of this liquid be allowed to diffuse itself through hydrogen, carbonic oxide, or any other combustible gas, it confers upon it the property of taking fire spontaneously when mixed with atmospheric air or with oxygen.

(456) *Solid Phosphide of hydrogen* ( $HP_2$ ).—The liquid phosphide is immediately decomposed by hydrochloric acid, and the solid yellow phosphide of hydrogen is formed. This substance is readily prepared by treating phosphide of calcium (649) with hot hydrochloric acid. It is insoluble in water and in alcohol. When heated with a solution of potassic hydrate the compound is dissolved, and phosphuretted hydrogen gas is liberated. There appear to be two varieties of the solid phosphide, one of a yellow, the other of a green colour; they do not differ from each other in composition. The solid yellow hydride of phosphorus takes fire at about  $302^\circ$  ( $150^\circ$  C.).

(457) *CHLORIDES OF PHOSPHORUS*.—With chlorine phosphorus forms two compounds, a trichloride,  $PCl_3$ , corresponding to phos-



phorous anhydride, and a pentachloride,  $\text{PCl}_5$ , which corresponds to phosphoric anhydride. So strong is the chemical attraction between these elements, that in an atmosphere of chlorine, phosphorus immediately takes fire. The following table shows the composition of these chlorides, and of two of their derivatives:—

		In 100 parts.			
		Phosph.	Chlorine.	Oxygen.	Sulphur.
Trichloride of phosphorus	$\text{PCl}_3 = 137.5$	22.54	77.46		
Pentachloride	$\text{PCl}_5 = 208.5$	14.86	85.14		
Oxytrichloride	$\text{POCl}_3 = 153.5$	20.19	69.38	10.43	
Sulphotrichloride	$\text{PSCl}_3 = 169.5$	18.28	62.84		18.88

(458) *Trichloride, or Terchloride of phosphorus; Phosphorous chloride* ( $\text{PCl}_3 = 137.5$ ); *Sp. Gr. of Vapour, Theoretic, 4.750; Observed, 4.875; of Liquid, 1.616 at 32° (0° C.); Boiling-pt. 173° 3 (78° 5 C.); Mol. Vol.*  ; *Rel. wt. 68.75.*—This liquid is sometimes prepared by causing the vapour of phosphorus to pass over corrosive sublimate placed in a long tube, and gently heated; but it may be obtained more easily and abundantly by transmitting a gentle stream of perfectly dry chlorine gas through dry and melted phosphorus contained in a retort; the operation may be conducted in the same manner as in the preparation of the chloride of sulphur (fig. 318); the trichloride distils as a very volatile, transparent, colourless, fuming liquid. It dissolves phosphorus freely, and is itself soluble in benzol and in carbonic disulphide: alcohol and ether decompose it with evolution of great heat, giving rise to various new compounds. It is also immediately decomposed by a large excess of water, and forms phosphorous and hydrochloric acids;  $\text{PCl}_3 + 3\text{H}_2\text{O}$ , yielding  $\text{H}_3\text{PO}_3 + 3\text{HCl}$ . Trichloride of phosphorus absorbs chlorine greedily, and is converted into the pentachloride; at a boiling temperature it also absorbs oxygen and furnishes the oxytrichloride.

(459) *Pentachloride or Perchloride of phosphorus; Phosphoric chloride* ( $\text{PCl}_5 = 208.5$ ); *Theoretic Sp. Gr. of Vapour, 3.601; Observed, at 572° (300° C.), 3.654. Rel. wt. 52.1; Mol. Vol.*  

—This compound\* is obtained by placing dry phosphorus in a flask provided with a stopcock, exhausting the air, and allowing chlorine to enter so long as it is absorbed; or it may be formed

\* The vapour volume of this compound is anomalous. Pentachloride of phosphorus may be supposed to be formed by the union of equal volumes of chlorine, and the vapour of the trichloride (Cahours). In a large number of cases where two bodies combine in the proportion of equal volumes of their components, no condensation occurs, as was long since indicated by Gay-Lussac.

by treating trichloride of phosphorus in a tall glass with an excess of chlorine. Pentachloride of phosphorus is also now prepared on a considerable scale by dissolving phosphorus in carbonic disulphide and transmitting dried chlorine in excess through the solution which is cooled artificially during the operation; the pentachloride is deposited in crystals from the solution on evaporation. It forms a white crystalline solid, which volatilizes below  $100^{\circ}\text{C}$ . whilst still solid, but it may be fused under pressure. In the flame of a lamp it burns, producing chlorine and phosphoric anhydride: with ammonia it combines readily. It is very deliquescent, and by a large excess of water is immediately decomposed into phosphoric and hydrochloric acids;  $\text{PCl}_5 + 4\text{H}_2\text{O}$  forming  $\text{H}_3\text{PO}_4 + 5\text{HCl}$ .

(460) *Phosphoryl chloride, Phosphoric oxytrichloride; or Oxychloride of phosphorus* ( $\text{POCl}_3 = 153.5$ ; *Rel. wt.* 76.75); *Sp. Gr. of Liquid*, 1.7; *of Vapour*, 5.298; *Boiling-pt.*  $230^{\circ}$  ( $110^{\circ}\text{C}$ .); *Mol. Vol.* [ ]—This compound is formed when the vapour of water is allowed to mingle slowly with that of the pentachloride, hydrochloric acid and oxychloride of phosphorus being the result. The reaction is as follows:  $\text{PCl}_5 + \text{H}_2\text{O} = \text{POCl}_3 + 2\text{HCl}$ . The oxychloride is a limpid, volatile, fuming liquid, which is decomposed by the further addition of water into phosphoric and hydrochloric acids.

Phosphoric oxytrichloride may be obtained with facility by Gerhardt's plan of distilling 1 part of crystallized boracic acid with  $4\frac{1}{2}$  parts of phosphoric chloride, when the following reaction occurs:  $3\text{PCl}_5 + 2(\text{HBO}_2, \text{H}_2\text{O}) = 3\text{POCl}_3 + 6\text{HCl} + \text{B}_2\text{O}_3$ . The oxychloride is readily condensed, whilst hydrochloric acid passes off in the form of gas, leaving boracic anhydride in the retort. Crystallized oxalic acid may be substituted for boracic acid in this operation, but it does not answer quite so well. The oxychloride may also be prepared by heating the pentachloride with phosphoric anhydride;  $3\text{PCl}_5 + \text{P}_2\text{O}_5 = 5\text{POCl}_3$ .

Both the chlorides and the oxychloride of phosphorus have been extensively used in the preparation of various organic substitution-products, particularly the oxychlorides and anhydrides of the organic acids.

(461) *Phosphoric sulphotrichloride, or Sulphochloride of phosphorus* [ $\text{PSCl}_3 = 169.5$ ; *Sp. Gr. of Liquid*, 1.631; *of Vapour*, 5.878; *Mol. Vol.* [ ]; *Rel. wt.* 84.75; *Boiling-pt.*  $257^{\circ}$  ( $125^{\circ}\text{C}$ .)], is a compound corresponding to the oxytrichloride, but containing sulphur instead of oxygen. It is obtained by decomposing phosphoric chloride with sulphuretted hydrogen:  $\text{PCl}_5 + \text{H}_2\text{S}$ , yielding  $\text{PSCl}_3 + 2\text{HCl}$ . It may be procured still more easily by the gradual addition of powdered antimonious sulphide to phosphoric chloride:

$3\text{PCl}_3 + \text{Sb}_2\text{S}_3 = 3\text{PSCl}_2 + 2\text{SbCl}_3$ . Sulphotrichloride of phosphorus is a fuming, colourless liquid, which, if heated with a solution of caustic soda in excess, exchanges its chlorine for oxygen; sodic chloride is formed, and a trisodic *sulphoryphosphate* may be obtained in six-sided tabular crystals which contain  $12\text{H}_2\text{O}$ . The composition of this salt is analogous to that of the trisodic phosphate, but the two are not isomorphous. The following equation explains the changes which accompany its production (Wurtz);  $\text{PSCl}_2 + 6\text{NaHO} = \text{Na}_3\text{PSO}_3 + 3\text{NaCl} + 3\text{H}_2\text{O}$ . Corresponding compounds with barium, calcium, and strontium may be formed by double decomposition with the sodium salt; they are white and insoluble.

(462) BROMIDES OF PHOSPHORUS.—*A Tribromide* [ $\text{PBr}_3$ ; *Sp. Gr.* at  $32^\circ$  ( $0^\circ$  C.), 2.925; *Boiling-pt.*  $347.5^\circ$  ( $175.3^\circ$  C.)], *Pentabromide* and *Oxybromide* of phosphorus, analogous to the corresponding compounds with chlorine, may be formed by similar methods.

(463) IODIDES OF PHOSPHORUS.—Two iodides of phosphorus may be formed, viz., a diiodide and a triiodide (Corenwinder, *Ann. de Chimie*, III. xxx. 242). The *Diiodide* ( $\text{PI}_2=285$ ) may be obtained by dissolving 1 part (or 1 atom) of phosphorus in carbonic disulphide, and adding  $8\frac{1}{2}$  parts (or 2 atoms) of iodine by cooling the mixture artificially, thin flexible prismatic crystals of the iodide are deposited, of a bright orange colour. This iodide melts at  $230^\circ$  ( $110^\circ$  C.), and is decomposed by water, hydriodic acid being one of the products.

*Phosphorous iodide*, or *Triiodide of phosphorus* ( $\text{PI}_3=412$ ).—This compound may be obtained in a manner similar to the last, by dissolving 1 part of phosphorus and  $12\frac{1}{2}$  parts of iodine in carbonic disulphide; the liquid is concentrated by evaporation, and on cooling it by a freezing mixture, dark red, six-sided plates are formed; it melts between  $122^\circ$  and  $131^\circ$  ( $50^\circ$  and  $55^\circ$  C.), and on cooling crystallizes in fine prisms. It deliquesces rapidly when exposed to the air.

Brodie (*Q. J. Chem. Soc.* v. 289) finds that iodine, when heated with phosphorus in the proportion of 1 atom of iodine to 100 atoms of phosphorus, converts nearly the whole of the phosphorus into the red variety described by Schrötter. When phosphorus was placed in a long tube, and heated till it just melted, and iodine was projected gradually into the phosphorus, the iodine was dissolved, colouring the phosphorus slightly red; when heated by an oil-bath to  $212^\circ$  ( $100^\circ$  C.), the colour became deep red; and between  $248^\circ$  and  $266^\circ$  ( $120^\circ$  and  $130^\circ$  C.), a scarlet powder was deposited on the sides of the tube; at  $284^\circ$  ( $140^\circ$  C.) the mass was quite solid, and on raising the heat to  $392^\circ$  ( $200^\circ$  C.), a sharp explosion took place: a sudden evolution of heat occurred, and the cork which closed the tube was blown out by the vapour of phosphorus. The red mass may be distilled in closed tubes, and when it is condensed in the cooler portions of the tubes it is

still in the red modification. The changes which occur in the process are supposed to be the following: first, the formation of diiodide of phosphorus; next, the transformation of this iodide by heat into an allotropic iodide; and thirdly, the decomposition of this new iodide into red phosphorus and a volatile iodide, which acts upon a further portion of the phosphorus; and thus the action is indefinitely continued.

(464) PHOSPHAM ( $\text{HN}_3\text{P}$ ).—If phosphorous chloride be cooled by a freezing mixture, and saturated with ammoniacal gas, a white saline mass ( $5\text{H}_3\text{N}, \text{PCl}_4$ ) is obtained; it is to be introduced into a tube of Bohemian glass, and heated to redness in a current of dry carbonic anhydride as long as any sal ammoniac is sublimed: a yellowish-white bulky amorphous powder remains behind: this substance is Rose's *phosphide of nitrogen*; but there can be no doubt that it contains hydrogen, it is the *phospham* of Gerhardt; probably its composition should be represented by the formula given above. In closed vessels it sustains a red heat without fusion or volatilization, but when heated in air it is slowly oxidized, with formation of phosphoric anhydride; if projected into fused potassic hydrate, it is decomposed with incandescence, tripotassic phosphate being formed, whilst ammonia and nitrogen are disengaged: but it is remarkable that dry chlorine and hydrochloric acid gases, and the vapour of sulphur, are without action upon it, even at a red heat; and it is but very slowly attacked by concentrated nitric acid. Solutions of the alkalis exert scarcely any action upon it. When heated in hydrogen, ammonia is formed. It combines with sulphuretted hydrogen, and if heated in a current of this gas, the new compound as it is formed is slowly sublimed in the form of a white powder. See also Gladstone (*J. Chem. Soc.*, 1864, 225; 1865, 1; 1866, 1 and 290).

(465) SULPHIDES OF PHOSPHORUS.—Sulphur and phosphorus may be melted together in all proportions: several definite compounds exist between them, corresponding in composition with the oxides of phosphorus; and in addition to these, a combination,  $\text{PS}_2$ , may be formed (Berzelius). All the sulphides of phosphorus are more fusible than either element separately, and are exceedingly inflammable; most of them may be obtained in crystals. They combine with the sulphides of the alkali-metals, and form a series of definite salts. The combination of sulphur with phosphorus should be gradually effected under warm water; great heat is extricated by their union, and the experiment requires to be conducted very carefully, in order to avoid explosion.

## CHAPTER IX.

### SILICON AND BORON.

#### § I. SILICON, OR SILICIUM: $\text{Si}=28$ : *Tetrad, as in $\text{SiCl}_4$ .*

(466) *Analogies of the Silicon Group.*—Silicon presents a certain analogy with boron in its tendency to unite with fluorine and with nitrogen. Silicon likewise exhibits a similar resemblance to titanium and tin not only in these particulars, but in its power of forming an oxide with 2 atoms of oxygen, and in its production of a volatile liquid tetrachloride. The double fluorides which

these elements form with the same bodies are isomorphous (*e.g.*,  $\text{SrF}_2, \text{SiF}_4, 2\text{H}_2\text{O}$ ;  $\text{SrF}_2, \text{SnF}_4, 2\text{H}_2\text{O}$ ;  $\text{SrF}_2, \text{TiF}_4, 2\text{H}_2\text{O}$ ). Zirconium forms a solid tetrachloride, but in properties it is nearly allied to silicon. These elements might be arranged thus in series:—

Silicon		Tin
Titanium		Zirconium.

These elements all belong to the class of tetrads, being equivalent in their most usual combinations to 4 atoms of hydrogen.

(467) SILICON when in combination with oxygen is the most abundant solid component of the earth's crust. It is the essential constituent of *Silex* or flint, and hence the origin of the term silicon. In order to obtain the element in its uncombined form, a mixture of fluor-spar with fine quartzose sand or ground flints is heated with concentrated sulphuric acid; a gaseous tetrafluoride of silicon is formed, which is partially soluble in water, producing an acid solution. This acid liquid, when neutralized with a solution of caustic potash, yields a sparingly soluble salt ( $2\text{KF}, \text{SiF}_4$ ). This potassic silicofluoride is to be thoroughly dried, and mixed in a glass or iron tube with eight or nine-tenths of its weight of potassium, and heated. Potassic fluoride is formed, whilst silicon is reduced and partially combined with the excess of potassium;  $2\text{KF}, \text{SiF}_4 + 2\text{K} = \text{Si} + 6\text{KF}$ . The mass, when cold, is treated with cold water, which produces a copious extrication of hydrogen gas, owing to the decomposition of the water by the excess of potassium. The washing with cold water is continued so long as any alkaline reaction upon test-paper is observed; when this ceases, it may finally be well washed with boiling water, so long as anything is dissolved. Sodium may be advantageously substituted for potassium in this experiment, in the proportion of 1 part of sodium to 2 of the silicofluoride. Silicon may also be obtained by heating, in a current of the vapour of silicic chloride, potassium or sodium placed in porcelain trays, in a glass tube, which it is best to protect by lining it with thin plates of mica.

Silicon may be obtained in two distinct modifications, *viz.*, the *amorphous* and the *crystalline* modification.

1. *Amorphous Silicon*.—When procured by the processes above described, silicon presents the appearance of a dull brown powder, insoluble in water, in which it sinks. It is a non-conductor of electricity; it soils the fingers when touched; it is not acted upon by nitric or sulphuric acid, but is readily soluble in hydrofluoric acid, and in a warm solution of caustic potash. When heated in air or in oxygen it burns brilliantly, and is converted into silica,

which fuses from the intense heat emitted, and forms a superficial coating over the unburnt silicon.

2. *Crystalline Silicon*.—The brown powder just described, if heated intensely in a closed platinum crucible, parts with a trace of hydrogen, shrinks greatly, becomes much denser, and darker in colour, and undergoes a remarkable change in properties. After such ignition, the silicon may be heated strongly in air or in oxygen, even when urged in the blowpipe flame, without taking fire: it has become sufficiently heavy to sink in oil of vitriol, and it resists the action of pure hydrofluoric acid, although if treated with a mixture of nitric and hydrofluoric acids it is rapidly dissolved. It may even be fused with nitre or with potassic chlorate without undergoing oxidation; but if the heat be urged to whiteness, the silicon burns brilliantly in the nitre; the oxidation, however, is much hastened by the addition of a little potassic carbonate; the mixture then deflagrates briskly, even though it may be at a much lower temperature: by fusion with potassic carbonate alone, silicon is easily and completely oxidized; in both cases silica is formed, and is immediately dissolved by the melted alkaline carbonate, from which it displaces a portion of carbonic anhydride. The properties of this compact form of silicon much resemble the *graphitoid* modification described by Deville and by Wöhler, who obtained the silicon in crystalline plates, by treating an alloy of silicon and aluminum in succession with boiling hydrochloric and hydrofluoric acids,\* when the silicon remains behind in the form of plates, which have a sp. gr. of 2.49,† and a metallic lustre. It may also be obtained by fusing 1 part of aluminum with 5 of glass free from lead, and 10 of powdered cryolite, treating the black mass with hydrochloric acid, and then with hydrofluoric. In this form silicon is a conductor of electricity; it may be heated to whiteness in a current of oxygen without undergoing change, but it is gradually dissolved by a mixture of hydrofluoric and nitric acids, though it is oxidized but very slowly when fused with potassic hydrate. When heated in a

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\* Silicon appears to have the same sort of tendency to combine with aluminum that carbon has to unite with iron. The alloy is easily formed by heating aluminum in a Hessian crucible with from 20 to 40 times its weight of dry potassic silicofluoride, fusing the two together for a quarter of an hour, and then allowing the crucible to cool slowly.

† Prof. W. H. Miller has shown (*Proceed. Roy. Soc.* xv. 11) that the plates of so-called *graphitoid* silicon are really only modifications of the octohedral form, in which two parallel faces are much larger than any of the other faces, while two other parallel faces are either too small to be observed, or are altogether wanting.

current of hydrochloric acid, a volatile liquid, chloro-leukon ( $\text{Si}_3\text{H}_4\text{Cl}_{10}$ ?) is formed (477), whilst hydrogen gas is liberated.

According to Deville (*Ann. de Chimie*, III. xlix. 65), silicon requires for its fusion a temperature between the melting-point of cast iron and that of steel. In order to fuse it he introduces the silicon into a platinum crucible lined with lime and protected by an outer clay crucible: the whole is then intensely heated in a wind furnace. If the lining of lime cracks, and the silicon reaches the platinum, the crucible is spoiled, owing to the formation of a platinum silicide. Fused silicon may also be procured when the mixture of sodic chloride with reduced silicon (obtained by igniting sodium in the vapour of silicic chloride), detached as far as possible from adhering fragments of porcelain, is placed in a crucible lined with charcoal, and exposed to intense heat in a forge; the sodic chloride becomes volatilized, and the silicon is fused into globules in the midst of the melted glass. These globules frequently show well-marked indications of crystallization; they have a dark, steel-grey colour, and a lustre like that of specular iron ore: now and then the silicon is found crystallized in regular double six-sided pyramids. It may also be obtained in regular six-sided prisms, terminated by three-sided pyramids, derived from the octohedron, by exposing pure aluminum in porcelain trays, heated intensely in a porcelain tube, to a current of the vapour of silicic chloride: the aluminum is volatilized as aluminic chloride, leaving the silicon in crystals which have a reddish lustre; they are hard enough even to cut glass like the diamond. Crystals of silicon may likewise be procured, and with less difficulty, by heating an earthen crucible to redness, and introducing a mixture of 3 parts of potassic silicofluoride with 1 part of sodium, cut into small pieces, and 4 of pure granulated zinc. The mixture must be maintained at a red heat, but below the temperature necessary to volatilize the zinc, until the slag is completely melted: it must then be allowed to cool slowly. The mass of zinc thus obtained contains long needles of silicon formed of octohedra, inserted one into the other: much of the zinc may be extracted by partial fusion at a low temperature, and the zinc which runs from the pasty mass in which the silicon is retained may be employed again in a similar operation: the zinc which still adheres to the silicon may be removed by digestion, first in hydrochloric, and afterwards in boiling nitric acid. If a very high temperature be employed in this operation the whole of the zinc may be expelled, and the silicon obtained in the fused condition. Deville and Caron have in this way (*Ann. de Chimie*, III. lxvii. 440) fused several hundred

grammes of silicon under a layer of potassic silicofluoride at a temperature near that at which cast iron melts, and they have cast it into large cylindrical bars without sensible loss by oxidation. These bars exhibited a brilliant surface, which was not altered by exposure to air.

Silicon forms with oxygen but a single oxide, the well-known compound, silica, or silicic anhydride.

Wöhler has, however, discovered a remarkable series of compounds into the composition of which both oxygen and hydrogen enter: one of these he calls *silicon* ( $\text{Si}_6\text{H}_6\text{O}_4$ ?) reserving the term *silicium* for the element; another he has named *leukon*,  $\text{Si}_3\text{H}_4\text{O}_5$ ; these bodies are evidently analogous to those obtained by Brodie from graphite (*note*, p. 73).

(468) SILICIC ANHYDRIDE or *Silica*; *Silicic dioxide* ( $\text{SiO}_2=60$ ); *Sp. Gr. cryst.* 2·642; *Amorphous* 2·2—2·3; *Comp. in 100 parts*, Si, 46·66; O, 53·34.—Berzelius represented this compound as a trioxide, giving the atomic weight of silicon as 22, if that of oxygen be 8. There are, however, reasons which render it more probable that it contains only 2 atoms of oxygen, and that it corresponds in composition to carbonic anhydride: for example, 1 atom of silicic chloride, when converted into vapour, instead of forming an exception to the general rule, as it does upon the theory of Berzelius, would then produce 2 volumes of vapour as usual: and in decomposing fused potassic carbonate by the addition of finely divided silica, it is found that the whole of the carbonic anhydride is expelled when the proportion of silica is to the carbonate as 60 to 138.\* This view has the advantage of greater simplicity, and it will be employed in this work. According to the experiments of Dumas, 100 parts of silica contain 46·7 of silicon, and 53·3 of oxygen.

Silica occurs in two modifications, the crystalline and the amorphous. In the crystalline state it has the higher specific gravity.

Pure crystalline silica occurs in *rock crystal* and in some forms of *quartz*, crystallized in six-sided prisms, transversely striated, and terminated by six-sided pyramids. *Amethyst* is a purple variety coloured with oxide of iron (ferric acid?). Silica is found nearly pure in *agate* and *calcedony*, which consist of a

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\* The experiments of Colonel Yorke (*Phil. Trans.* 1857) have, however, shown that the proportion of carbonic anhydride expelled by equal weights of silica from an excess of the different carbonates, varies with the nature of the base; sodic carbonate losing a larger proportion than potassic carbonate, and lithic carbonate more than sodic carbonate, where equal quantities of silica were employed.



mixture of the crystallized and amorphous varieties. *Calcedony* in alternate layers of different colours constitutes *onyx*. *Carnelian* is a red or brown variety containing ferric oxide. *Flint* is a variety of calcedony, chiefly found in the upper chalk; and *opal* consists of the amorphous variety of silica with a varying quantity of water. Silica constitutes the principal ingredient of all sandstones; and it enters largely into the composition of felspar, and of a vast variety of minerals. Pure crystallized silica is perfectly transparent and colourless; in hardness it approaches the precious gems. A heat as intense as that of the oxyhydrogen blowpipe is required for its fusion; it then melts to a transparent glass, which may be drawn out into fine, flexible, elastic threads of the amorphous variety. Native silica is insoluble in water, and in all acids except the hydrofluoric.

*Preparation.*—Finely divided silica has the aspect of a white earth, but though insoluble it possesses the power of uniting with bases, as is shown by the usual process of obtaining it in a state of purity:—A mixture of potassic and sodic carbonates is fused by a red heat, and one-third of its weight of ground flint, or some other siliceous mineral in fine powder, is added in small quantities to the melted mass; on each addition a brisk effervescence, due to the escape of carbonic anhydride, takes place; the mixture is then heated strongly for some minutes. It is afterwards allowed to cool, and if digested in water the mass is slowly dissolved, with the exception of a portion of the impurities, such as ferric oxide and titanic anhydride, which the siliceous material may have contained. A larger quantity of silica than that above indicated would still yield a mixture which might be fused by a strong heat; but it becomes less soluble in proportion to the excess of silica, till at length a point is reached at which it is no longer soluble in water or in the common acids; indeed, it forms the basis of glass. When it is proposed to obtain pure silica, however, an excess of alkali is always used: the resulting compound is then easily attacked by acids, in which it is wholly dissolved, if the acid be dilute and in sufficient quantity. If the solution in hydrochloric acid be evaporated, the silica is separated as a gelatinous hydrate, which, by continuing the heat, is converted into a white earthy-looking powder no longer soluble in acids: after being digested with oil of vitriol to remove traces of titanic anhydride, and decanting the strong acid, it must be well washed as long as anything is dissolved; if then dried and ignited, it is perfectly pure. As thus procured, silica, like charcoal and other porous bodies, absorbs aqueous vapour rapidly from the air, without becoming sensibly moist.

Perfectly pure silica may also be procured by transmitting the gaseous silicic fluoride into water; a partial decomposition of the gas occurs, and one-third of its silicon is oxidized and deposited in white hydrated flocculi, which, if washed and ignited, furnish silica of snowy whiteness;  $3\text{SiF}_4 + 2\text{H}_2\text{O}$ , yielding  $\text{SiO}_2 + 2(2\text{HF}, \text{SiF}_4)$ . Silica may likewise be obtained nearly pure by heating colourless quartz to redness, and quenching it in water; the mineral is rendered friable by this treatment, and is then easily reduced to a fine powder: common flints treated in a similar manner give a very white powder, which is nearly pure silica. All the artificial forms of silica are amorphous, and are much more easily attacked by solvents than the crystalline variety.

(469) *Hydrates of Silica*.—Insoluble, however, as silica generally is in water, and though silica, when once deposited, even in the gelatinous form, is almost insoluble either in water or in acids, a modification of it exists which may be dissolved completely at the moment of its liberation from some of its compounds which are already in solution. For instance, if a dilute solution of an alkaline silicate be poured into a considerable excess of hydrochloric acid, the whole of the silica is retained in solution; but it may be precipitated from this acid solution by the gradual addition of a solution of potash, so as to neutralize the acid; and if to a solution of an alkaline silicate in water hydrochloric acid be added gradually, the silica is precipitated in a gelatinous form in proportion as the alkali is neutralized.

From the solution of alkaline silicate in excess of hydrochloric acid, Graham obtains a pure solution of hydrated silica, by subjecting the liquid to dialysis in a hoop dialyser of parchment-paper (62). If a stratum of liquid 4 tenths of an inch (1 centimetre) in depth be subjected for 4 or 5 days to dialysis, changing the water in the outer vessel at intervals of 24 hours, the hydrochloric acid and the soluble chlorides will be found to have diffused so completely that the liquid in the dialyser will give no precipitate with argentic nitrate.

A solution may thus be obtained containing 5 per cent. of silica, and it may be concentrated till the quantity of silica reaches 14 per cent. if the liquid be boiled down in a flask. In open vessels it is apt to gelatinize on the edge, and the whole then solidifies. The solution is tasteless, limpid, and colourless, with a feebly acid reaction, rather greater than that of carbonic acid; 100 parts of silica require 1·85 of potash ( $\text{K}_2\text{O}$ ) to neutralize this effect on litmus. The solution is not easily preserved for many days, as it becomes converted into a solid transparent jelly which, even in closed vessels, shrinks, whilst water is separated from it. The coagulation is retarded by hydrochloric acid, and by small quantities of caustic potash or soda. Sulphuric, nitric, and acetic acids are without action on the solution, but it is slowly coagulated by a few bubbles of carbonic anhydride. Its coagulation is also effected in a few minutes by the addition of  $\frac{1}{100}$  part of any alkaline or earthy carbonate in solution, but not by caustic ammonia nor by neutral nor acid salts. Alcohol and sugar, gum and caramel, are without action, but solutions of gelatin, soluble alumina, and soluble

ferric oxide, immediately cause a gelatinous precipitate: when solution of silica is gradually added to one of gelatin in excess, the precipitate obtained consists of 100 of silica and 92 of gelatin. (*Phil. Trans.* 1861, p. 204.)

By evaporation *in vacuo* at  $59^{\circ}$  ( $15^{\circ}$  C.), the silica is left behind in the form of a transparent glassy mass of great lustre, containing, after exposure for two days over sulphuric acid, 21.99 of water, which corresponds nearly to the formula  $\text{H}_2\text{O}, \text{SiO}_2$ .

There is, however, considerable difficulty in obtaining a definite hydrate of silica, for it easily loses a portion of its water at low temperatures, and is moreover a very hygroscopic substance. Ebelen, by the action of moist air upon silicic ether, obtained a transparent, glassy hydrate, which had a composition represented by the formula  $3\text{H}_2\text{O}, 2\text{SiO}_2$ ; and a compound which gave similar results on analysis was procured by Doveri, on drying the ordinary gelatinous hydrate of silica *in vacuo* over sulphuric acid without the aid of heat. Fuchs obtained two hydrates of silica, one containing from 9.1 to 9.6 per cent. of water, corresponding to the formula  $\text{H}_2\text{O}, 3\text{SiO}_2$ , which requires 9.1 per cent., the other between 6.6 and 7 per cent., agreeing nearly with the formula  $\text{H}_2\text{O}, 4\text{SiO}_2$ , which would contain 6.9 per cent. of water. From the occurrence of a mixed ether consisting of  $(\text{C}_5\text{H}_{11}3\text{C}_2\text{H}_5, \text{SiO}_2)$ , it appears that the silicic is really a tetrabasic acid, though from the facility with which its basic hydrogen escapes as water, the composition of the hydrate is doubtful.

A very white and light hydrate of silica occurs naturally in abundance in beds situated at the base of the chalk formation, between the upper greensand and the gault: the proportion of hydrated silica in these deposits varies very greatly, ranging from 5 to as much as 72 per cent., being most abundant in the upper portion of the deposit (Way). A mixture of this material with slaked lime, when made into a paste with water, is in a few weeks converted into a silicate of lime, and the change is accelerated by the presence of 2 or 3 per cent. of soda.

Insoluble silica may be gradually converted into the soluble variety by long digestion with solutions of the alkalis. Even flints in their unground condition may be dissolved in strong solutions of caustic alkali (sp. gr. 1.16), if the solution be digested upon them under pressure at a temperature of between  $302^{\circ}$  and  $392^{\circ}$  ( $150^{\circ}$  and  $200^{\circ}$  C.).

Finely divided hydrate of silica is also dissolved by the alkaline carbonates: these carbonates are only partially decomposed by the silica which is dissolved. It appears to be owing to the solubility of silica in solutions of the carbonates that almost all spring and river waters contain silica in solution in minute quantity; on evaporation the silica is obtained in the insoluble form. When the action of the alkaline liquid is aided by that of a high temperature, as is the case with the Geysers or boiling springs of

Iceland, very large quantities of silica are dissolved, which, as the liquid cools, are deposited as 'petrifications' on surrounding objects exposed in the basin or in the stream.

Silica also exists in the soluble form in a class of minerals termed zeolites, which are hydrated siliceous compounds (670) found in the cavities of the amygdaloid rocks. The zeolites, if finely powdered, and treated with hydrochloric acid, swell up to a transparent jelly; this gelatinous mass consists of hydrate of silica.

These observations on the various conditions under which silica may be rendered soluble derive their interest from the extensive formation of crystallized silica, so abundantly diffused over the surface of the earth, and the difficulty of crystallizing it by artificial means. The zeolites may have been obtained by deposition from solution; quartz and agate by crystallization from an aqueous solution.

(470) *Silicates*.—The silicates are most abundant natural productions. All the forms of clay, felspar, mica, hornblende, and a large number of other common minerals, are compounds of this description.

Silica combines with bases in several different proportions; most of its compounds are found in the form of crystallized minerals, many of which are double silicates of very complex composition. It is highly probable that silicic, like phosphoric acid, admits of modifications which differ in basic power. Odling (*Phil. Mag.* Nov. 1859) proposes to call the silicates of the type  $M_4SiO_4$ , *orthosilicates*; those of the type  $M_2SiO_3$ , *metasilicates*, with an intermediate class formed by the combination of one atom of each of the two. The combinations with bases which are of most usual occurrence belong to one or other of the following classes, the orthosilicates being regarded as the *normal salts*:—

Orthosilicates	{	Diopase ... ..	$Cu^+H_2SiO_4$
$M'SiO_4$ or	{	Olivine ... ..	$(MgFe)''SiO_4$
$N''_2SiO_4$	{	Forge cinder ... ..	$Fe''_2SiO_4$
Metasilicates	{	Wollastonite ... ..	$Ca''SiO_3$
$M'_2SiO_3$ or	{	Picrosmine ... ..	$2(Mg''SiO_3), H_2O$
$N''SiO_3$	{	Augite ... ..	$(CaMg)''SiO_3$
$\frac{2}{3}$ Silicates	{	Meerschäum ... ..	$Mg''_2SiO_4, 2(SiO_2, H_2O)$
$M'_4SiO_4, 2SiO_2$	{	Silicate of calcium ... ..	$Ca''_2SiO_4, 2SiO_2$
Acid silicates	{	The composition of many of the ordinary varieties of glass may be approximatively represented by mixtures of different silicates which have this formula.	
$M'_2SiO_3, SiO_2$ or	{		
$N''SiO_3, SiO_2$	{		

In the above formulæ  $M'$  stands for 1 atom of any metallic monad, such as potassium, and  $N''$  for 1 atom of any metallic dyad, such as calcium.

In most cases, however, in the formulæ of the silicates I shall adhere to the custom of representing them as compounds of the bases with the anhydride silica. Their diversified forms have not hitherto been satisfactorily classified.

Most of the silicates are fusible ; their fusibility is increased by mixture with each other ; those which contain readily fusible oxides melt at the lowest temperature, and in general the basic silicates fuse more readily than those which are normal in composition, or which contain excess of silica. All the silicates are insoluble in water, with the exception of those of the alkalis which contain a large proportion of base. The hydrated silicates, and those which contain the largest proportion of base, are those most easily decomposed by acids ; but the anhydrous normal and acid silicates of the earths are not decomposed by any acid except the hydrofluoric. The silicates may be detected by fusing them with sodic or potassic carbonate, and then heating the residue with acid, and evaporating to dryness ; on treating what is left with hot water, the silica remains undissolved in the form of a white powder, which, when fused with sodic carbonate upon platinum foil before the blowpipe, yields a colourless bead of glass. The freedom of silica from bases may be ascertained by its being volatilized without residue when evaporated in platinum with pure hydrofluoric acid in excess. Pure silica is not attacked by fusion with microcosmic salt, but is left as a spongy mass in the clear bead ; if any earth or base be present, the bead is generally more or less opalescent. Borax dissolves silica slowly, when fused with it, forming a clear colourless bead.

The acid character is so feebly marked in silica, that the ordinary vegetable acids, such as the acetic, the oxalic, and the tartaric, precipitate silica from its combinations with the alkalis ; and a current of gaseous carbonic anhydride, or even the gradual absorption of carbonic acid from the atmosphere, produces a similar result. At a high temperature, however, the action is reversed ; for as silica is not volatilized to any perceptible extent by the heat of a furnace, it decomposes the carbonates and the salts of all the volatile acids when ignited with them ; hence even the sulphates yield up their bases to the silica, whilst the sulphuric anhydride is expelled.

(471) If coarsely-powdered calcic silicide (649a) be digested in fuming nitric acid, in a vessel kept cool by immersion in water, an extrication of hydrogen takes place, and a new compound is gradually formed ; to this Wöhler has given the name of *silicon*, which is objectionable, because it has been already appropriated to the element itself. The mixture is to be agitated frequently and kept for some time in a dark place until no further extrication of gas occurs. The

mixture is then to be diluted with 7 or 8 parts of water, and the insoluble material collected, washed, pressed between blotting paper, and dried in the dark *in vacuo*, over sulphuric acid.

*Silicone* ( $\text{Si}_2\text{H}_4\text{O}_4$  ?), or *chryseon*, as it might be fitly termed in allusion to its colour, is a bright orange-yellow mass, insoluble in water, alcohol, carbonic disulphide, phosphorous chloride, or silicic chloride. When heated it deepens in colour, and afterwards takes fire with slight explosion and the emission of sparks, leaving silica, which is brown, owing to the presence of silicon. If heated without access of air, it evolves hydrogen, leaving a residue of silica and amorphous silicon in shining brown flakes. The decomposition begins even at  $212^\circ$  ( $100^\circ \text{C.}$ ). If heated with water in a sealed tube to  $384^\circ\text{.8}$  ( $196^\circ \text{C.}$ ) it is speedily converted into white flakes of silica, whilst pure hydrogen is evolved, and is retained under great pressure in the tube.

In the dark it may be preserved without alteration, either in a moist or dry state; but if exposed to diffused daylight it slowly becomes paler, with evolution of hydrogen. If exposed to the sun's rays under water, it immediately begins to evolve hydrogen, and a white residue is left, which Wöhler has termed leukon.

Silicone is not attacked by chlorine nor by fuming nitric or sulphuric acid, even when boiling: hydrofluoric acid dissolves it completely. But its characteristic reaction is the rapid manner in which it is dissolved by solutions of the caustic alkalis, with rise of temperature and violent extrication of hydrogen. Ammonia, even in very dilute solutions, has a similar effect. The carbonates of the alkali-metals dissolve it more slowly. Silicone acts as a powerful reducing agent, especially in the presence of alkalis. Salts of copper, gold, silver, palladium, and osmium yield with it dark silicates of a suboxide.

(471a) *Leukon* ( $\text{Si}_2\text{H}_4\text{O}_4$  ?), Wöhler (*Lieb. Ann.* cxxvii. 268).—This compound was first described as a hydrated oxide of silicon, but it has subsequently been further examined by Wöhler, who has changed its name to leukon, in allusion to its aspect (from *λευκός* white).

Leukon at temperatures above  $32^\circ$  ( $0^\circ \text{C.}$ ), when in contact with water, undergoes oxidation, and evolves hydrogen. Wöhler and Buff (*Ann. de Chimie*, III. lii. 276) describe this body as a snow-white powder when dry, sufficiently light to float upon water, though it sinks in ether. The caustic alkalis and their carbonates dissolve it rapidly with brisk effervescence, owing to the formation of a silicate of the base, whilst hydrogen escapes. Ammonia also decomposes it with slow evolution of hydrogen. The acids, with the exception of the hydrofluoric, do not act upon it. It may be heated in air to  $572^\circ$  ( $300^\circ \text{C.}$ ) without alteration; but at a somewhat higher temperature it takes fire, burning with scintillation, and emitting a phosphorescent light, at the same time giving off hydrogen gas, which burns explosively. If heated in a closed crucible it is decomposed into a mixture of silicon and silica; silicic hydride (472) being liberated, but undergoing immediate decomposition. Leukon is slightly soluble in water, but the liquid quickly undergoes decomposition, evolving hydrogen gas. The solution exerts a strong reducing power, precipitating gold and palladium from neutral solutions of their salts, in a metallic form. It also instantly bleaches a solution of potassic permanganate; and throws down reduced selenium and tellurium, from solutions of selenious and tellurous acids in hydrochloric acid. Wöhler and Buff, however, think it probable that this solution contains a still lower oxide of silicon than the one above described.

Leukon is best prepared by placing crystallized silicon in a wide glass tube connected with a U-tube cooled by a mixture of ice and salt, whilst the apparatus terminates in a bent tube dipping into ice-cold water; the silicon is to be raised to a barely visible red heat, and a current of dry hydrochloric acid gas transmitted; chloroleukon ( $\text{Si}_2\text{H}_4\text{Cl}_4$ ) is formed and in part condensed in the U-tube,

and the portion which passes on is immediately decomposed by the water into hydrochloric acid and a white powder;  $\text{Si}_2\text{H}_4\text{Cl}_2 + 5\text{H}_2\text{O}$  becoming  $\text{Si}_2\text{H}_4\text{O}_2 + 10\text{HCl}$ . The voluminous white precipitate thus formed consists of leukon, and is to be quickly pressed between folds of blotting-paper and dried *in vacuo* over sulphuric acid.

(472) **SILICIC HYDRIDE** ( $\text{H}_4\text{Si}?$ ).—Along with the foregoing compound, Wöhler and Buff have also described a remarkable gaseous combination of hydrogen and silicon. It has not been procured in a pure state, but may be obtained mixed with a large quantity of free hydrogen as a spontaneously inflammable gas, when a wire or plate of aluminum combined with silicon is placed in a solution of sodic chloride and made the positive pole of a feeble voltaic battery. A large surface of aluminum and the avoidance of any considerable elevation of temperature are necessary to insure the maximum production of the hydride.

The electrolytic gas is colourless; when allowed to burn in the air, it emits white fumes, consisting of amorphous silica. If a cold plate of porcelain or of glass be introduced into a jet of the burning gas, a brown film of reduced silicon is deposited upon its surface. It is also decomposed by transmission through a glass tube heated to redness, when a coating of reduced silicon is deposited, and the gas is found to have lost its self-lighting power. Its exact composition is not known. This gas precipitates many metallic solutions, such as cupric sulphate, argentic nitrate, and palladious chloride; but it is without action upon the solutions of lead and of platinum; the precipitates in most cases contain silicon.

Hydride of silicon may also be obtained by decomposing with cold diluted hydrochloric acid an impure silicide of magnesium obtained by mixing intimately 40 parts of fused magnesian chloride, 35 of dried sodic silicofluoride, and 10 of fused sodic chloride; these are mixed in a warm dry tube, with 20 parts of sodium in small fragments, and thrown into a red-hot Hessian crucible, which is immediately covered; the heating is to be continued till the vapours of sodium cease to burn.

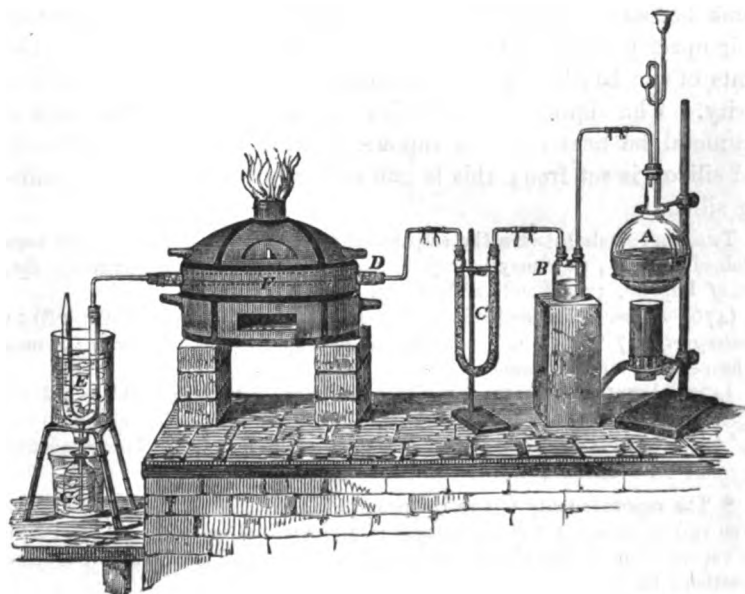
(473) **SILICIC NITRIDE** or **NITRIDE OF SILICON** may be obtained by the direct action of nitrogen upon silicon at a very high temperature; crystallized silicon, when heated in nitrogen gas, becoming coated with a light, bluish, fibrous compound of the two elements. This nitride may be heated to redness in chlorine without undergoing decomposition. When heated to full redness in a current of steam, ammonia is disengaged abundantly and silica is formed.

(474) **SILICIC SULPHIDE**: ( $\text{SiS}_2=92$ ).—A disulphide corre-

sponding in composition to silica is formed by transmitting the vapour of carbonic disulphide over a mixture of finely divided silica and carbon : and when either compact or pulverulent silicon is strongly heated in an atmosphere of sulphur, combustion occurs with a red glow ; a white earthy-looking disulphide, which absorbs moisture rapidly from the air, is the result : this compound is completely soluble in water, but it is decomposed whilst undergoing solution ;  $\text{SiS}_2 + 2\text{H}_2\text{O}$  becoming  $\text{SiO}_2 + 2\text{H}_2\text{S}$  ; sulphuretted hydrogen and soluble silica being formed : the silica may be obtained as a jelly by evaporation.

(475) CHLORIDE OF SILICON ; *Silicic chloride* ; ( $\text{SiCl}_4 = 170$ ) ; *Mol. Vol.*   ; *Rel. wt.* 85 ; *Theoretic Sp. Gr. of Vapour*, 5·873 ; *Observed*, 5·939 ; *of Liquid*, 1·5237 at  $32^\circ$  ( $0^\circ \text{C.}$ ) ; *Boiling-pt.*  $138^\circ\cdot 2$  ( $59^\circ \text{C.}$ ).—This compound may be formed by heating silicon in chlorine ; but in practice it is obtained by the following indirect method :—Finely powdered silica is made up into a paste with oil and charcoal, and heated in a covered crucible ; the charred mass in fragments is transferred to a porcelain tube, in which it is ignited, and subjected to a current of dry chlorine :

FIG. 321.



neither chlorine nor carbon separately can decompose silica, but together they effect its decomposition easily, carbonic oxide escaping, whilst silicic chloride is formed ;  $\text{SiO}_2 + 2\text{Cl}_2 + \text{C}_2 =$



$2\text{CO} + \text{SiCl}_4$ . The product is received into vessels cooled with a freezing-mixture.

Fig. 321 shows a form of apparatus by which the chloride may be readily prepared: D is a porcelain tube, which contains the mixture of charcoal and silica; chlorine is liberated from the flask A, washed with water in B, dried by transmitting it over pumice and sulphuric acid contained in the tube C, and allowed to pass through the tube D, which with its contents is exposed to a red heat in the furnace; silicic chloride distils over into the bent tube, E, where it is condensed by immersion in a freezing-mixture of ice and salt; a tube fused into the bend of the tube E, conveys the chloride into a bottle, G, which may also be kept cool by ice.

Silicic chloride is a transparent, colourless liquid, with a pungent, acid, irritating odour; it is very volatile, and fumes strongly in the air. Its composition is the following:—

		By weight.	By volume.	Sp. gr.
Chlorine	... $\text{Cl}_4$	$= 142$ or $83\cdot53$	$4$ or $2\cdot0$	$= 4\cdot906$
Silicon	... $\text{Si}$	$= 28$	$2\frac{1}{2}$ or $1\frac{1}{2}$	$= 0\cdot967$
Silicic chloride	$\text{SiCl}_4$	$= 170$ $100\cdot00$	$2$ $1\cdot0$	$= 5\cdot873$

Water immediately decomposes silicic chloride, depositing hydrated silica, and forming hydrochloric acid. A moist atmosphere also decomposes the chloride, causing the deposition of silica in opaque lamellar plates, which like the mineral *hydropbane* become transparent when immersed in water, but resume their opacity on drying: the siliceous deposit obtained from the joints of the bamboo, known as *tabasheer*, exhibits the same peculiarity. The liquid chloride does not act on potassium, but if the metal be heated in its vapour, potassic chloride is produced, and silicon is set free; this is one of the best methods of obtaining silicon.

Two compounds between the sulphide and the chloride of silicon have been obtained (Pierre); they may be represented by the formulæ  $(\text{SiS}_2)_2\text{SiCl}_4$ ; *Sp. Gr. of Vapour*,  $5\cdot24$ \* and  $(2\text{SiS}_2)_3\text{SiCl}_4$ .

(476) *Silicic Bromide*  $[\text{SiBr}_4]$ ; *Sp. Gr. of Liquid at 32° (0° C.)*  $2\cdot813$ ; *Boiling-pt.*  $307\cdot4$  ( $153^\circ\text{C.}$ ) is analogous in properties to the chloride: it may be formed in a similar manner.

(477) **HYDROCHLORATE OF CHLORIDE OF SILICON**; *Chloroleukon*;  $(\text{Si}_2\text{H}_4\text{Cl}_{10}$  or  $4\text{HCl}, 3\text{SiCl}_4 = 443)$ ; *Sp. Gr. of Liquid*,  $1\cdot65$ ; *Boiling-pt.*  $107\cdot6$  ( $42^\circ\text{C.}$ ); (Wöhler and Buff, *Annal. de Chimie*, III. lii. 269).—This compound

\* The vapour-density of this compound is anomalous, for the formula above given corresponds to 3 volumes instead of 2 volumes of vapour, or 1 volume of the vapour of disulphide of silicon and 2 of the tetrachloride united without condensation; for

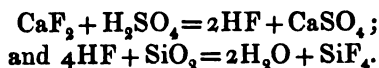
		By volume.	Sp. gr.
$\text{SiS}_2$	$=$	$1$ or $0\cdot33$	$= 3\cdot959$
$2\text{SiCl}_4$	$=$	$2$ $0\cdot67$	$= 1\cdot059$
		$3$ $1\cdot00$	$5\cdot018$

is a colourless, highly mobile liquid, which fumes powerfully on exposure to the air, depositing a white film upon surrounding bodies, and emitting a vapour of suffocating odour. It is highly inflammable, and burns with a greenish, feebly luminous flame, depositing silica and emitting hydrochloric acid. If its vapour be mixed with oxygen, it explodes violently on the transmission of the electric spark, silica being deposited, whilst hydrochloric acid and silicic chloride are formed. The liquid may be boiled upon sodium without undergoing decomposition. If passed through a tube heated to redness, it is decomposed into a mixture of silicic chloride and hydrochloric acid, whilst half its silicon is deposited in the form of a brown amorphous crust exhibiting a metallic lustre. Water decomposes it immediately with great elevation of temperature, leucon and hydrochloric acid being formed:  $\text{Si}_2\text{H}_4\text{Cl}_{10} + 5\text{H}_2\text{O}$  yielding  $\text{Si}_2\text{H}_4\text{O}_4 + 10\text{HCl}$ .

The mode of preparing this compound by transmitting dry hydrochloric acid over crystallized silicon heated to dull redness, has already been described when speaking of the preparation of leucon (471a).

A similar liquid compound ( $\text{Si}_2\text{H}_4\text{Br}_{10}$ ?; *Sp. Gr.* 2.5) may be obtained in like manner by means of hydrobromic acid. The corresponding compound of iodine ( $\text{Si}_2\text{H}_4\text{I}_{10}$ ?) forms a fusible, crystalline solid.

(478) FLUORIDE OF SILICON; *Silicic tetrafluoride* ( $\text{SiF}_4 = 104$ ); *Rel. wt.*, 52; *Theoretic Sp. Gr.*, 3.593; *Observed*, 3.60; *Mol. Vol.* [ ]—The fluoride is one of the most remarkable compounds of silicon: so powerful is the attraction between fluorine and silicon that hydrofluoric acid separates silicon from its most intimate combinations, such as silica and glass. In order to prepare silicic fluoride, equal parts of finely-powdered fluor-spar and siliceous sand, or powdered glass, are mixed in a capacious flask or retort, with twelve times their weight of oil of vitriol. On the application of heat, a colourless gas, with a peculiar, pungent, acid odour, is given off; hydrofluoric acid is liberated, and this immediately attacks the silica, as is shown in the following representation of the reaction:—



The composition of the gas may be thus represented:—

			By weight.	By vol.	Sp. gr.
Silicon	... Si	=	28 or 26.9	2 <sup>2</sup> or 1 <sup>2</sup>	= 0.967
Fluorine	... F <sub>4</sub>	=	76    73.1	4    2	= 2.626
Silicic fluoride	SiF <sub>4</sub>	=	104    100.0	2    1	= 3.593

Silicic tetrafluoride fumes strongly in the air; it is not inflammable, but extinguishes a lighted taper; under strong pressure it was liquefied by Faraday; and according to Natterer it becomes solid at  $-220^\circ$  ( $-140^\circ \text{C.}$ ). The gas is dissolved and partially decomposed by water; it must therefore be collected over mercury, and in jars which have been perfectly dried at a high temperature; the slightest trace of moisture on the surface of the jar causes a deposition of silica, which adheres very firmly to

the glass, and renders it opalescent. Silicic fluoride combines with twice its volume of ammoniacal gas, and forms with it a crystalline volatile compound.

(479) SILICOFLUORIC ACID; *Hydrofluosilicic Acid* ( $2\text{HF}, \text{SiF}_4 = 144$ ).—When a stream of gaseous silicic fluoride is transmitted through water, it is partially decomposed and partially dissolved. Two atoms of water react on 3 of the fluoride, and produce the silicofluoric acid, which is dissolved, whilst one-third of its silicon is deposited as silica in the form of hydrate:—



In the preparation of this acid the tube from which the fluoride is escaping must not plunge at once into water, other-

FIG. 322.



wise it will speedily become obstructed by the deposited silica. This inconvenience may be prevented by placing a little mercury at the bottom of the vessel, in order that the tube may dip beneath the mercury, as shown in fig. 322. Each bubble as it rises becomes surrounded by a siliceous envelope, and finally the liquid sets into a gelatinous mass: the acid liquid is separated by pressure in linen from the deposit, which when freed from adhering

acid, constitutes a pure hydrate of silica. A more easy method of obtaining the acid, when it is required in quantity, consists in dissolving silica in diluted hydrofluoric acid.

A saturated solution of silicofluoric acid forms a very sour, fuming liquid. In solution it does not attack glass, but it does so if allowed to evaporate upon it; silicic fluoride becomes volatilized, leaving free hydrofluoric acid, which, reacting on the silica, produces water and silicic fluoride, as in the ordinary process for making that gas;  $4\text{HF} + \text{SiO}_2 = 2\text{H}_2\text{O} + \text{SiF}_4$ .

Silicofluoric acid combines with bases to form salts, if the base be not added in excess; if an excess of base be employed, silica is precipitated, and the whole of the fluorine is separated as a metallic fluoride. In the first case the action may be thus represented:  $2\text{KHO} + 2\text{HF}, \text{SiF}_4 = 2\text{H}_2\text{O} + 2\text{KF}, \text{SiF}_4$ . In the

second case:  $6\text{KHO} + 2\text{HF}, \text{SiF}_4 = 4\text{H}_2\text{O} + 6\text{KF} + \text{SiO}_2$ . A dilute solution of silicofluoric acid produces transparent jelly-like precipitates in the salts of the alkali-metals; it is frequently employed as a precipitant of potassium. With salts of barium the acid gives a white crystalline precipitate.

§ II. BORON: B=10.9: *Triad, as in*  $\text{BCl}_3$ .

(480) BORON is the characteristic combustible element of the acid contained in borax, whence it derives its name. In nature it is always met with in combination with oxygen. It is a body which occurs in comparatively sparing quantities, and only in a few localities. Though one of the triad elements, it presents considerable analogy with silicon in its properties, and its mode of combination: it may be obtained in the crystalline, and the amorphous state.

*Amorphous Boron.*—Berzelius isolated boron by a process analogous to that employed in the case of silicon. Potassic borofluoride ( $\text{KF}, \text{BF}_3$ ) a sparingly soluble salt, is made by saturating hydrofluoric with boracic acid, neutralizing the liquid with potassic carbonate, and washing the compound with cold water: it is then dried at a heat a little below redness. When cold it is mixed with an equal weight of potassium, and heated in a covered iron crucible,  $2(\text{KF}, \text{BF}_3) + 3\text{K}_2 = 8\text{KF} + 2\text{B}$ . The potassic fluoride is removed by hot water.

Boron as thus obtained is an amorphous, dull olive-green powder, which, before it has been strongly ignited, soils the fingers, and is dissolved by pure water in small quantity, forming a greenish yellow solution; from which, however, it is precipitated unchanged on adding a little solution of sal ammoniac. Boron is not oxidized by exposure to air, to water, or to solutions of the alkalis, whether cold or boiling. It is, however, easily oxidized when treated with nitric acid or with aqua regia. After exposure to intense heat in vessels from which air is excluded, it becomes denser, and darker in colour. It may be fused by the application of a heat still more intense than that required to melt silicon. As first obtained, boron exhibits a strong attraction for oxygen, and, if heated in air or in oxygen, takes fire below redness, burning with a reddish light and emitting vivid scintillations; it is thus converted superficially into boracic anhydride, which melts and protects a portion of the boron. If mixed with nitre and heated to redness, it deflagrates powerfully. It is also oxidized when ignited with potassic hydrate; and when heated with potassic carbonate in fusion it sets carbon free, and

potassic borate is formed. Pulverulent boron, like silicon, is a non-conductor of electricity.

Boron may be obtained in the amorphous form in large quantity by the following method (Wöhler and Deville; *Liebig's Annal.* cv. 67):—150 grammes of fused boracic anhydride is coarsely powdered and mixed rapidly with 90 grms. of sodium cut into small pieces. The mixture is then introduced into a cast-iron crucible previously heated to bright redness; 70 or 80 grms. of solid but previously fused sodic chloride are placed upon the top of the mixture, and the crucible is covered. As soon as the reaction is over, the still liquid mass is thoroughly stirred with an iron rod, and poured, whilst red hot, in a slender stream into a large and deep vessel containing water acidulated with hydrochloric acid. The pulverulent boron is then collected on a filter and washed with acidulated water till the boracic acid is got rid of; after which the washing may be continued with pure water, until the boron begins to run through the filter. It must finally be dried upon a porous slab without the application of heat.

*Crystallized Boron.*—In order to convert the amorphous into the crystallized form, the following method may be adopted:—A small Hessian crucible is lined with the pulverulent boron made into a paste with water, and the boron is pressed in strongly, as in the ordinary mode of lining a crucible with charcoal. In the central cavity a piece of aluminum weighing from 6 to 9 grammes is placed; the cover is luted on and the crucible enclosed in a second, the interval between the two being filled with recently ignited powdered charcoal. The outer crucible is next closed with a luted cover, and the whole exposed for a couple of hours to a heat sufficient to fuse nickel. The temperature is then allowed to fall; and when cold the contents of the inner crucible are digested in diluted hydrochloric acid, which dissolves out the aluminum; beautiful crystals of boron are left, generally transparent, but of a dark brown colour. A quantity of scales of so called *graphitoid* boron, an alloy of boron with aluminum,  $B_2Al$  (Wöhler), are formed at the same time, in pale, copper-coloured, opaque plates.

Crystallized boron has a sp. gr. of 2.68; it assumes the form of transparent octohedra belonging to the pyramidal system (?). These crystals when pure are nearly colourless, but they usually contain considerable amounts of aluminum and carbon: they refract light powerfully, and are hard enough to scratch the ruby, and even sensibly to wear away the diamond. Crystallized boron burns imperfectly in oxygen when heated to full whiteness, and becomes coated with a layer of fused boracic anhydride. It however burns easily when heated to redness in dry gaseous chlorine, becoming converted into the gaseous boric trichloride. No acid or mixture of acids has any action upon crystalline boron.

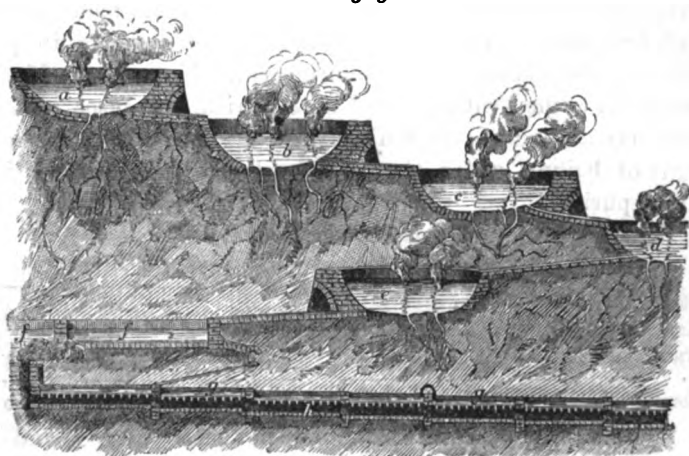
Boron, like titanium, enters into direct combination with nitrogen at a high temperature; a quantity of this nitride is formed as a grey coherent mass during the preparation of crystallized boron. Pulverulent boron, when heated in a current of dry ammoniacal gas, becomes incandescent, and is converted into nitride, whilst hydrogen is liberated. Boron in all its forms burns freely in chlorine; when ignited in contact with steam,

with sulphuretted hydrogen, and with hydrochloric acid, it decomposes them, but the latter is attacked with some difficulty; boracic acid, boric sulphide, and boric chloride being formed respectively, whilst hydrogen is liberated.

(481) BORACIC ANHYDRIDE; *Boric sesquioxide* ( $B_2O_3=69.8$ ); *Crystallized Boric acid* ( $HBO_2, H_2O$ ).—This is the only known compound of oxygen and boron. It is found combined with sodium as an acid borate in the *tincal* obtained from Thibet, and in a crystallized borate of calcium and magnesium from the western coast of South America; quite recently borax and boracic acid have been found in California; but its most abundant source is the maremma of Tuscany, where it is met with in the uncombined state, and accompanied by sulphuretted hydrogen: it issues in small quantity along with the jets of steam (*fumerolles* or *soffioni*), maintained by the action of subterranean fire.

These, at Monte Cerboli and Monte Rotondo, in Tuscany, are directed into small lagoons or artificial basins, such as those shown in fig. 323, the waters of

FIG. 323.



which on evaporation yield a crude boracic acid, from which a large proportion of the borax of commerce is now manufactured. According to the ingenious suggestion of Lardarello, the heat supplied by the fumerolles themselves is employed in this evaporation. Water from the adjacent springs is directed into the uppermost basin, *a*; here it stays for twenty-four hours, and is run off after successive intervals of twenty-four hours into each of the four lower basins, *b*, *c*, *d*, *e*. From the last of these it flows into settling vats, *f*, *f*, where in the course of twenty-four hours more the suspended matters subside. The supernatant liquid, which contains from  $1\frac{1}{2}$  to 2 per cent. of boracic acid, is then decanted into shallow leaden evaporating pans, *g*, *g*, heated by the vapours of several fumerolles, which circulate underneath in flues, *h*, arranged for the purpose. In twenty-four hours the liquor is reduced to about half its bulk; it is then transferred to a smaller pan, on a lower level, where it is allowed to eva-

porate for twenty-four hours longer: it is again transferred to a smaller pan, where after the lapse of twenty-four hours more it has acquired a density of 1·07 or 1·08, and is sufficiently concentrated to crystallize on cooling. Calcic sulphate is deposited in abundance in the pans during these evaporations, and it requires removal from time to time. About two thousand tons of the crude acid are annually thus procured in Tuscany. The crude acid, however, seldom contains more than three-fourths of its weight of the pure crystallized acid, the remainder consisting principally of ammoniac and magnesian sulphates, with small quantities of aluminic sulphate and of other alkaline and earthy sulphates, a peculiar organic matter, and a small proportion of silica. By boring into the volcanic strata, artificial soffioni have been formed which, as at Travale, yield a large quantity of boracic acid, by treatment similar to that above described.

The commercial acid is purified by adding to it sodic carbonate as long as effervescence occurs, and thus forming borax, which is obtained nearly pure by crystallization (592).

In order to procure the acid, purified borax is dissolved in 4 parts of boiling water, and to the hot solution, oil of vitriol equal in weight to that of one-fourth of the borax employed is added after dilution with a little water. In this process sodic sulphate is formed, and boracic acid is liberated. The sparingly soluble boracic acid crystallizes out on cooling, in pearly-looking scales which feel greasy to the touch. It is not, however, quite pure, as it always retains a little sulphuric acid. To remove this, the crystals are washed with ice-cold water, dried, and fused in a platinum crucible, and on redissolving the mass in 4 times its weight of boiling water, the acid crystallizes, on cooling, in a state of purity.

The composition of this acid is the following;—

Anhydride.			Crystallized : $\text{HBO}_2, \text{H}_2\text{O}$ .		
Boron	... $\text{B}_2$	= 21·8 or 31·23	B	= 10·9 or	} 56·39
Oxygen	... $\text{O}_3$	= 48      68·77	$\frac{1}{2}\text{O}_3$	= 24·0	
Water	...		$1\frac{1}{2}\text{H}_2\text{O}$	= 27·0	43·61
<hr/>			<hr/>		
Boracic acid	$\text{B}_2\text{O}_3$	= 69·8      100·00	$\text{BH}_2\text{O}_3$	= 61·9      100·00	

*Properties.*—The crystals of boracic acid effloresce and lose two-thirds of their water at a gentle heat, and at a slight increase of temperature become converted into the anhydride; at a red heat, or a little below, the anhydride fuses to a transparent, viscid, ductile glass, which remains clear as it cools. It gradually absorbs moisture from the air and crumbles to pieces. Boracic acid communicates to its compounds the property of ready fusibility: indeed it is chiefly on this account that it is valued. Many of the borates are admirably adapted for fluxes, which are used in the glazing of porcelain, and in the melting of gold and silver.

Boracic acid is sparingly soluble in cold water, but it is dissolved by 3 times its weight of boiling water: the solution has a

bitterish and scarcely sour taste; if allowed to evaporate upon turmeric paper, it turns the paper brown, as an alkali would do; it gives to litmus a purplish-red tint, instead of the usual bright red of the stronger acids. It gradually decomposes solutions of the carbonates even in the cold; but, on the other hand, a brisk current of gaseous carbonic anhydride or of sulphuretted hydrogen will cause a separation of boracic acid in crystals from a strong solution of borax. Boracic acid is soluble in alcohol, and the solution burns with a characteristic green flame, which, when viewed through the spectroscope is seen to exhibit five well marked green bands (Part I. fig. 81, No. 6). It is not possible to evaporate a solution of boracic acid either in alcohol or in water without losing a portion of the acid, for the vapour always carries with it an appreciable amount of the acid; and if steam at a high temperature be transmitted over boracic acid or calcic borate, the acid is volatilized in considerable quantities.

*Borates.*—Boracic anhydride is but very slowly volatilized by ignition, and hence, though its chemical activity is very feeble, it at high temperatures expels all anhydrides more volatile than itself, when fused with their salts. It enters into combination with the alkaline bases in a great variety of proportions, resembling silica in this respect as in some others. Although many of these salts contain more than 1 atom of acid, they all restore the colour of reddened litmus-paper. A potassic hexaborate ( $K_2O, 6B_2O_3, 5H_2O$ ) may be obtained in crystals, and a triborate ( $K_2O, 3B_2O_3, 8H_2O$ ) has also been crystallized. The borates of the alkali-metals are freely soluble, those of the other metals are only imperfectly soluble; none of the borates, however, are so insoluble as to furnish an accurate mode of ascertaining the quantity of boracic acid present in solution by the formation of a precipitate. All the sparingly soluble borates are dissolved by diluted nitric acid. In analysing a borate it is usual to determine the amount of all the other acids and metals, and other constituents, and to estimate the deficiency as boracic acid. It is not unlikely that boracic acid may have been overlooked in many minerals, as its detection in small quantities is rather difficult except by the aid of the spectroscope. If a borate be fused with a little hydropotassic sulphate mixed with a fourth of its weight of finely powdered fluor-spar on a platinum wire in a Bunsen gas-flame, its transient green light is easily analysed by the prism.

(482) A *sesquisulphide*, a *trichloride*, and a *tribromide* of boron may be prepared by methods similar to those employed to obtain the corresponding compounds of silicon. *Boric trichloride* ( $BCl_3 = 117.4$ ; *Sp. Gr.* 3.942;



*Mol. Vol.* [ ] ; *Rel. wt.* 58·7) ; is gaseous at ordinary temperatures ; it fumes strongly in air, and is instantly decomposed by water into hydrochloric and boric acids. It has the following composition :—

			By weight.		By volume		Sp. gr.
Boron ...	B	=	10·9 or 9·29		2 P or 0·5	=	0·376
Chlorine ...	Cl <sub>3</sub>	=	106·5    90·71		3    1·5	=	3·679
Boric chloride	BCl <sub>3</sub>	=	117·4    100·00		2    1	=	4·055

Two volumes of this trichloride unite with 3 volumes of ammonia, and become condensed into a volatile crystalline saline body.

(483) BORIC FLUORIDE, or *Trifluoride of boron* (BF<sub>3</sub>=67·9) ; *Rel. wt.* 33·9 ; *Sp. Gr.* 2·312 ; *Mol. Vol.* [ ] .—Boron forms with fluorine a compound somewhat analogous to the silicic fluoride. It is best prepared as follows : 2 parts of fluor-spar and 1 of vitrified boracic anhydride, both in fine powder, are intimately mixed, and intensely ignited in a wrought-iron tube closed at one end ; decomposition occurs thus :  $3\text{CaF}_2 + 4\text{B}_2\text{O}_3 = 3(\text{Ca } 2\text{BO}_3) + 2\text{BF}_3$ . Calic diborate remains in the tube, and the trifluoride of boron passes over as a colourless gas, which may be collected over mercury. The composition of boric fluoride is the following :—

			By weight.		By vol.		Sp. gr.
Boron ...	B	=	10·9 or 16·07		2 P or 1 P	=	0·376
Fluorine ...	F <sub>3</sub>	=	57·0    83·93		3    1·5	=	1·969
Boric fluoride	BF <sub>3</sub>	=	67·9    100·00		2    1·0	=	2·345

Boric fluoride does not support combustion ; it has an irritating odour, and fumes densely in the air. It is instantly absorbed by water, which dissolves 700 times its volume of the gas, with rapid rise of temperature, whilst it increases in density to 1·77, and forms an oily-looking, fuming, and corrosive acid liquid, which chars organic matter as powerfully as oil of vitriol. This solution has been called *borofluoric acid*. The reaction which occurs when the gas comes into contact with water is very simple,  $2\text{BF}_3 + 3\text{H}_2\text{O}$ , yielding (B<sub>2</sub>O<sub>3</sub>,6HF). When heated, a part of the gas escapes, and the specific gravity of the liquid becomes reduced to 1·584 ; when of this density it distils unchanged, and contains two atoms of water, the formula of the aqueous solution becoming (B<sub>2</sub>O<sub>3</sub>,6HF,2H<sub>2</sub>O). Borofluoric acid is also easily prepared by saturating hydrofluoric acid with boracic acid, keeping the mixture cool, and then concentrating it in platinum vessels till dense fumes arise.

When largely diluted with water, one-fourth of the boron is separated in the form of boracic acid, and another compound is found in solution, termed *hydrofluoboric acid*. In composition this body somewhat resembles the silicofluoric acid, though it is not strictly analogous to it. Its formation is readily explained

by the following equation, from which it will be seen that hydrofluoboric acid contains the elements of 1 atom of hydrofluoric acid and 1 atom of boric tri-fluoride:—



So strong is the tendency to the formation of this compound in dilute solutions, that if boric acid be added to a solution of fluoride of potassium or of ammonium, for each equivalent of boric acid present, 3 equivalents of potash or of ammonia are liberated, and fluoboride of the base is formed: for example,  $8\text{KF} + 2\text{HBO}_3 + 2\text{H}_2\text{O} = 2(\text{KF}, \text{BF}_3) + 6\text{KHO}$ .

(484) BORIC NITRIDE, or NITRIDE OF BORON (BN).—As already mentioned, boron combines with nitrogen at a red heat with great avidity. Boric nitride may also be obtained by transmitting a current of dry nitrogen gas over a mixture of 1 part of pure finely-powdered charcoal with 4 parts of fused boracic anhydride, exposed to a full white heat in a porcelain tube. It may likewise be procured readily by mixing 1 part of anhydrous borax with 2 parts of sal ammoniac, and heating it to full redness in a covered platinum crucible; a white, infusible, porous mass is left, which, when boiled with diluted hydrochloric acid and well washed, yields boric nitride as a white, light, amorphous, insoluble powder, which feels like talc when rubbed upon the skin. It may be heated in hydrogen or in chlorine without change; it is but very slowly acted upon by concentrated acid or alkaline solutions; but when fused with potassic hydrate it is converted into ammonia and potassic borate,  $3\text{KHO} + \text{BN} = \text{KBO}_3 + \text{K}_2\text{O} + \text{H}_3\text{N}$ . In a current of steam it is completely converted into ammoniac borate;  $\text{BN} + 2\text{H}_2\text{O}$  yielding  $\text{H}_4\text{NBO}_3$ . It is also decomposed when heated with easily reducible metallic oxides, such as those of lead or copper; nitric oxide being evolved.

## CHAPTER X.

### OTHER COMPOUNDS OF THE NON-METALS.

#### § I. COMPOUNDS OF HYDROGEN AND OXYGEN.

(485) PEROXIDE OF HYDROGEN; *Hydric dioxide*, or *Hydroxyl* ( $\text{H}_2\text{O}_2=34$ ); *Sp. Gr. of Liquid*, 1.453.—Water is not the only compound of oxygen with hydrogen. Thénard in the year 1818, discovered a remarkable substance, which, as it contains 2 atoms of oxygen in combination with 2 atoms of hydrogen, is termed *peroxide of hydrogen*. It is a colourless liquid, of syrupy consistence, with an odour somewhat resembling that of chlorine very much diluted; it remains liquid at a temperature of  $-22^\circ$  ( $-30^\circ \text{C.}$ ). This peroxide is a very unstable compound; a temperature of about  $68^\circ$  ( $20^\circ \text{C.}$ ) is sufficient to cause the oxygen to begin to escape in small bubbles, and when heated to the boiling-point of water the gas is evolved with a rapidity almost amounting to an explosion. The liquid is soluble in water in all proportions; when diluted it is less easily destroyed by elevation of

temperature, though ebullition for a few minutes is sufficient to expel the whole of the additional atom of oxygen, water alone remaining. This circumstance furnishes an easy method of analysing the hydric peroxide. A given weight of the liquid is placed in a small retort, and diluted with 10 or 12 times its bulk of water; the temperature is raised to ebullition, oxygen is given off freely, and the gas is collected over mercury and measured when cool: the weight of the oxygen can be calculated from its bulk, and deducting the weight thus obtained from that of the peroxide operated upon, it will be found that for each 16 mgrms. of oxygen expelled, 18 of water remain; consequently, as water contains 2 mgrms. of hydrogen combined with 16 of oxygen, hydric peroxide will contain 2 mgrms. of hydrogen united with 32 of oxygen.

Hydric dioxide bleaches a solution of litmus, and many vegetable colours; a drop of it, if placed upon the tongue, blanches it, and destroys sensation for a time; the taste of the liquid is astringent and somewhat metallic. By means of hydric peroxide the black plumbic sulphide ( $\text{PbS}$ ) is converted into the white sulphate of the metal ( $\text{PbSO}_4$ ), and many metallic protoxides become oxidized to the maximum.

Hydric peroxide, however, is not only decomposed by substances which possess an attraction for oxygen, but the mere contact of many finely divided metals and metallic oxides which do not undergo any permanent change, occasions its decomposition; gold, silver, and platinum produce an instantaneous evolution of oxygen gas, which is the more rapid the finer the subdivision of the body by which the decomposition is occasioned. A similar effect is produced by contact with the oxides of these metals, or with the peroxide of manganese or of lead. It is especially to be remarked that the oxides of silver, gold, and platinum, not only decompose peroxide of hydrogen, but they are themselves reduced to the metallic state. These decompositions are all rendered less rapid by the addition of a few drops of sulphuric or hydrochloric acid, but are hastened by the addition of a little free alkali. If hydric peroxide in its concentrated form be allowed to fall drop by drop upon argentic oxide, black oxide of manganese, or upon metallic silver, platinum, or osmium in a finely divided state, it is decomposed with explosion and great elevation of temperature.

*Preparation.*—Owing to the unstable character of hydric peroxide, its preparation in a pure state is attended with great difficulty, although in principle the process is simple. An indirect

method is resorted to for procuring it:—Caustic baryta ( $\text{BaO}$ ), when heated to dull redness in a current of oxygen gas, combines with an additional atom of oxygen, and becomes baric dioxide ( $\text{BaO}_2$ ): when this substance is moistened with water it forms a hydrate ( $\text{BaO}_2 \cdot 6\text{H}_2\text{O}$ ). Hydric peroxide is obtained from this hydrated compound by decomposing it by means of hydrochloric acid.

The hydrated baric dioxide is reduced to a paste by grinding it in a mortar with water, and is added in small quantities at a time to hydrochloric acid diluted with water, and kept cool by immersing the vessel in ice and water; the dioxide is gradually dissolved without effervescence, baric chloride and peroxide of hydrogen being formed;  $\text{BaO}_2 \cdot 6\text{H}_2\text{O} + 2\text{HCl}$  yielding  $\text{H}_2\text{O}_2 + 6\text{H}_2\text{O} + \text{BaCl}_2$ . When the hydrochloric acid is nearly saturated with the dioxide, the baric chloride is decomposed by the cautious addition of diluted sulphuric acid; an insoluble baric sulphate is precipitated, whilst hydrochloric acid is set free, and is able to decompose a fresh quantity of baric dioxide, which must be added with the same precautions as at first. The addition of sulphuric acid produces no change on the hydric peroxide which is present in the solution: it is merely an expedient for getting rid of the barium and liberating the hydrochloric acid.\*

The baric sulphate is next removed by filtration, and the liquid thus left is simply a very dilute solution of hydric peroxide with an excess of hydrochloric acid. This acid is again able to decompose a fresh portion of the baric dioxide. The same series of operations is repeated upon the liquid three or four times in succession, alternately adding baric dioxide, and removing the barium in the form of baric sulphate; until a liquid is obtained which consists of dilute hydric peroxide containing 30 or 40 times its bulk of oxygen, and a large quantity of hydrochloric acid. The hydrochloric acid has now to be removed, and this is effected by adding argentic sulphate, until a trace only of hydrochloric acid is left in the liquid.† Sulphuric acid is thus substituted for the hydrochloric acid, which is precipitated in the form of the insoluble argentic chloride, while the hydric peroxide remains unchanged in the liquid.

The sulphuric acid is now got rid of by the careful addition of baryta water, which is at last added drop by drop, so as to remove the whole of the sulphuric acid without introducing any excess of baryta: the liquid is once more filtered, and is now a pure solution of hydric peroxide in water; finally, it may be transferred to a basin and placed over sulphuric acid in the exhausted receiver of the air-pump. The water evaporates much more rapidly than the peroxide, which is thus at length obtained in a concentrated form.

Schönbein has shown (*Ann. de Chimie*, III. lviii. 479) that in various processes where ozone is formed, small quantities of hydric peroxide are also produced; and in the electrolysis of acidulated and saline solutions when ozone is formed, traces of the peroxide are likewise produced if the operation is con-

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\* Pelouze substitutes silicofluoric for hydrochloric acid in decomposing the baric dioxide; it shortens the operation by removing the barium at once in the form of an insoluble baric silicofluoride. Baric dioxide may also be decomposed by suspending it in water, and transmitting a current of carbonic anhydride, but the solution so obtained is dilute.

† Oxide of silver cannot be substituted for the sulphate, as it would immediately occasion the evolution of the additional atom of oxygen in the compound.

ducted at a low temperature, the proportion of gaseous oxygen collected in the voltameter being then always a little below the theoretical quantity.

## § II. COMPOUNDS OF CARBON AND HYDROGEN.

(486) THE compounds of carbon with hydrogen are very numerous. They are all derived from the decomposition of bodies of organic origin. Many of these bodies exhibit absolute identity in the proportion of the two elements which compose them, although they are endowed with properties perfectly distinct; and, from the different densities of these bodies in the gaseous or vaporous condition, it is obvious that the condensation of their particles is different. For example, the following are a few of the many compounds which contain in 100 parts 85·71 of carbon and 14·29 of hydrogen:—

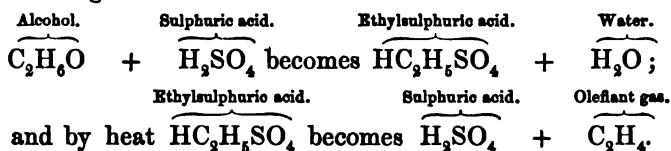
					Mol. vol.
Olefiant gas	...	$C_2H_4$	...	specific gravity, 0·978	... 2
Oil gas	...	$C_4H_8$	...	" "	1·852 ... 2
Naphthene	...	$C_8H_{16}$	...	" "	3·900 ... 2
Cetylene	...	$C_{16}H_{32}$	...	" "	8·007 ... 2

Such bodies are said to be *polymeric*. At present it will not be necessary to describe more than three compounds of carbon and hydrogen—viz., olefiant gas, marsh gas, and oil gas.

(487) OLEFIANT GAS; *Elayl*, or *Ethylene* ( $C_2H_4=28$ ); *Rel. wt.* 14; *Theoretic Sp. Gr.* 0·967; *Observed*, 0·9784; *Mol. Vol.*      .

*Preparation.*—1.—If 2 measures of concentrated sulphuric acid be mixed with 1 measure of alcohol, in a retort capable of containing at least four times the bulk of the liquid introduced, on distillation a transparent colourless gas is obtained, consisting of carbon and hydrogen. It is accompanied by the vapour of ether, and towards the close of the process by sulphurous acid in large quantity. The olefiant gas, as this compound of carbon and hydrogen is termed, at first comes off freely, but by degrees the mixture blackens and becomes thick, and froths up considerably, so that the operation requires careful watching in its latter stages: this tendency to frothing may be much diminished by adding to the mixture, before applying heat, a quantity of sand equal in weight to half that of the acid employed. The gas may be purified by causing it first to pass through an empty bottle, kept cool by immersion in water, in order to condense the vapours of alcohol and ether; then washing it in a solution of potash, to absorb sulphurous acid, removing the last traces of ether by allowing it to bubble up through concentrated sulphuric acid, and finally drying it, when necessary, by causing it to traverse a tube filled with fragments of pumice moistened with oil of vitriol.

This remarkable decomposition may be thus explained : alcohol enters into combination with sulphuric acid, and forms a peculiar compound acid, the sulphovinic or ethylsulphuric acid, which is decomposed by a high temperature : the sulphuric acid is liberated in an unchanged condition, whilst the alcohol breaks up into water and olefiant gas ; at the same time a portion of the water with which the acid was at first diluted distils off, and accompanies the olefiant gas :—



2.—Olefiant gas is also obtained, mixed with various other gaseous compounds, during the destructive distillation of a large number of bodies of organic origin—particularly the resins, the fats and oils, and the different varieties of pit-coal. It forms an important component of coal-gas.

*Properties.*—Olefiant gas is transparent and colourless ; it has a faint, sweetish, alliaceous odour, and is soluble in about 12 times its bulk of cold water. It was liquefied by Faraday under great pressure, but remained unfrozen at  $-166^\circ$  ( $-110^\circ$  C.) Olefiant gas does not support life or combustion, but is itself very inflammable, and burns with a white luminous flame, depositing carbon abundantly upon cold bodies which are introduced into its flame. If it be transmitted through porcelain tubes heated to bright redness, it is decomposed : half its carbon is deposited, and another compound of carbon with hydrogen (light carburetted hydrogen) is formed, which occupies the same volume as that of the olefiant gas from which it was produced. If the heat to which the gas is subjected be extremely intense, all the carbon is deposited, and for each volume of gas decomposed 2 volumes of hydrogen are liberated.

The composition of olefiant gas may be ascertained by detonation with oxygen : the explosion, however, is very powerful, and requires care, otherwise the eudiometer will be broken. One volume of the gas requires for its complete combustion 3 volumes of oxygen ; 2 volumes of carbonic anhydride remain and represent 2 out of the 3 volumes of oxygen, whilst the other volume of oxygen combines with 2 volumes of hydrogen, furnishing 2 volumes of steam, which immediately become condensed : 2 volumes of hydrogen and 2 of carbon vapour are therefore condensed in olefiant gas into the space of 1 volume.  $\text{C}_2\text{H}_4 + 3\text{O}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O}$ .

From these data the composition of the gas may be represented in the following manner:—

			By weight.	By vol.	Sp. gr.
Carbon	...	$C_2 =$	24 or 85.71	4 or 20 =	0.829
Hydrogen	...	$H_4 =$	4 14.29	4 20 =	0.138
Olefiant gas	...	$C_2H_4 =$	28 100.00	2 10	0.967

Olefiant gas is slightly soluble in alcohol, in oil of turpentine, and in the fixed oils. It combines with sulphuric anhydride, forming with it a peculiar compound; hence it is completely absorbed by fuming sulphuric acid, and it is somewhat soluble in ordinary oil of vitriol; the latter by brisk agitation with the gas may be made to take up 30 or 40 times its volume, forming ethylsulphuric acid. It also combines with, and is absorbed by, antimonious chloride. Olefiant gas, when mixed over water with an equal volume of chlorine, unites with it and becomes condensed to a heavy, sweetish, aromatic liquid: it collects into oily-looking drops, which sink in water: it was owing to this reaction that the name of olefiant (or oil-producing) gas was given to it, and the oily body itself is commonly known as *Dutch liquid*, from the circumstance of its discovery in Holland. If 1 measure of olefiant gas be mixed with 2 measures of chlorine, the mixture may be kindled by a lighted taper, and will burn quietly, depositing the whole of the carbon of the gas in the form of a dense smoke, whilst the hydrogen unites with the chlorine to form hydrochloric acid. Olefiant gas will be referred to hereafter among the products of organic chemistry; where, as a dyad radicle, it performs an important part.

(488) **DUTCH LIQUID**; *Glycol dichloride*, or *Ethylene dichloride* ( $C_2H_2Cl_2$ ,  $HCl$ , or  $C_2H_4Cl_2 = 99$ ). *Sp. Gr. of Liquid*, 1.28 at  $32^\circ$  ( $0^\circ$  C.); *of Vapour, Theoretic*, 3.42; *Observed*, 3.45; *Boiling-pt.*  $185^\circ$  ( $85^\circ$  C.); *Mol. Vol.*  ; *Rel. wt.* 49.5.—This is a compound of considerable interest, as it is the substance from which the chlorides of carbon were originally obtained by Faraday; and the careful study (since made by Regnault) of the stages by which these substances are formed, illustrates in a striking manner the mode in which compounds may be procured by a process of substitution in which the hydrogen of the original body is displaced by chlorine. Moreover its relation to the diatomic alcohol, glycol, has invested its study with additional importance.

*Preparation.*—I.—Dutch liquid is required in considerable quantity for these experiments; it may be easily obtained by

Limpriht's method of transmitting the olefiant gas through a mixture of black oxide of manganese and hydrochloric acid, from which the chlorine is generated. The olefiant gas is conveyed into this mixture by means of a bent tube which passes through the tubulure of the retort, and the Dutch liquid, as it is formed, distils over into a receiver connected with the retort. Formerly it was the practice to allow a current of chlorine and a current of olefiant gas, both in a moist state, to meet in a large glass globe, where they condensed each other under the influence of diffused daylight.

2.—Another method by which Dutch liquid may be prepared consists in transmitting olefiant gas through antimonious chloride ( $\text{SbCl}_3$ ) so long as it is absorbed. The product is submitted to distillation, and the heat is maintained so long as the distillate yields an oily liquid on the addition of water.

The oil which is obtained by either of these processes is decanted, agitated with successive portions of oil of vitriol so long as they become blackened, and the product purified by re-distillation.

Dutch liquid is a colourless aromatic liquid which is not soluble in water, but freely soluble in ether and in alcohol. The simplest supposition respecting the composition of this body, since its vapour consists of equal volumes of chlorine and olefiant gas, condensed into half their bulk, is that its atomic weight should be ( $\text{CH}_2\text{Cl}$ ), or one-half of that which has been given above (487). The investigations of Regnault have, however, shown that the composition of Dutch liquid is not correctly represented by so simple a formula; that its molecular formula is not  $\text{CH}_2\text{Cl}$ , but just double. The usual combining volume of an atom of such vapours is twice that of the atom of hydrogen, and the density of the vapour, as obtained by experiment (3.45) coincides almost exactly with that required by the supposition that the formula is ( $\text{C}_2\text{H}_4\text{Cl}_2$ ):—

			By weight.	By vol.	Sp. gr.
Chlorine ...	...	...	$\text{Cl}_2 = 71$ or $71.68$	2 or 1	$= 2.453$
Carbon ...	...	...	$\text{C}_2 = 24$	$4^p$ 2	$= 0.829$
Hydrogen ...	...	...	$\text{H}_4 = 4$	4 2	$= 0.138$
Dutch liquid ...	...	...	$\text{C}_2\text{H}_4\text{Cl}_2 = 99$	2 1	$= 3.420$

The formula for Dutch liquid is sometimes written  $\text{C}_2\text{H}_3\text{Cl.HCl}$ .

It was ascertained by Faraday that when Dutch liquid is exposed in a glass vessel with chlorine to the direct rays of the sun, taking care to renew the chlorine as long as it is absorbed, the liquid is ultimately converted into the white crystalline and vola-



tile chloride of carbon ( $C_2Cl_6$ ), whilst a very copious disengagement of hydrochloric acid gas takes place (387).

Regnault has shown that the formation of this chloride of carbon is the result of the interchange of chlorine for hydrogen in the composition of the Dutch liquid; so that the chloride of carbon may be regarded as Dutch liquid in which the place of the hydrogen is supplied by chlorine: and he has described a series of compounds intermediate between the liquid and Faraday's solid chloride of carbon. For example:—if chlorine be transmitted through Dutch liquid, the gas is absorbed rapidly, and the liquid acquires a yellow colour, which disappears with copious evolution of hydrochloric acid when it is brought into the sun's rays: by carefully adjusting the addition of chlorine, a new liquid is obtained, which boils at  $239^\circ$  ( $115^\circ$  C.), and has a specific gravity of 1.422. Two atoms or 1 molecule of chlorine act upon 1 molecule of Dutch liquid, 1 atom of the chlorine combining with 1 of hydrogen to form the disengaged hydrochloric acid, while the second atom of chlorine takes the position of the displaced hydrogen: thus  $C_2H_4Cl_2 + Cl_2$  furnish  $C_2H_3Cl_3 + HCl$ . This new liquid may be made to absorb a fresh quantity of chlorine, and in the sun's rays it undergoes a change analogous to the preceding one; a liquid is formed which boils at  $275^\circ$  ( $135^\circ$  C.), and has a density of 1.576;  $C_2H_3Cl_3 + Cl_2$  yielding  $C_2H_2Cl_4 + HCl$ . This third liquid, if again acted upon by two additional atoms of chlorine, undergoes a further similar decomposition; a still heavier liquid, of specific gravity 1.663, boiling at  $307^\circ.4$  ( $153^\circ$  C.), is produced,  $C_2H_2Cl_4 + Cl_2$  becoming  $C_2HCl_5 + HCl$ : and finally, this fourth liquid, when acted upon by an excess of chlorine, loses the remaining atom of hydrogen, and becomes Faraday's solid chloride of carbon; for  $C_2HCl_5 + Cl_2 = C_2Cl_6 + HCl$ ; the successive products having the composition and density indicated in the following table:—

*Chlorinated Compounds derived from Dutch Liquid.*

Name of compound.	Boiling point.		Specific gravity.		Formula.
	$^\circ$ C.	$^\circ$ F.	Liquid.	Vapour.	
Dutch liquid ... ..	85	185	1.280	3.45	$C_2H_4Cl_2$
Chlorinated ditto ... ..	115	239	1.422	4.613	$C_2H_3Cl_3$
Dichlorinated ditto ... ..	135	275	1.576	5.769	$C_2H_2Cl_4$
Trichlorinated ditto ... ..	153	307	1.663	7.08	$C_2HCl_5$
Solid chloride of carbon ... ..	180	356		8.157	$C_2Cl_6$

It will be seen that as the quantity of chlorine increases, the boiling-point rises, and the density both of the liquid and of the

vapour increases: in every case 1 atom of the compound yields 2 volumes of vapour.

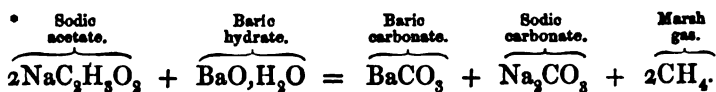
(489) *Glycol dibromide*, or *Ethylene dibromide* ( $C_2H_4Br_2 = 188$ ); *Sp. Gr. of Liquid*, 2.163; *of Vapour*, 6.485; *Fusing-pt.* about  $10^\circ$  ( $-12^\circ C.$ ); *Boiling-pt.*  $265^\circ$  ( $129^\circ.5 C.$ ); *Rel. wt.* 94.—Cahours has obtained from olefiant gas a series of compounds containing bromine: ethylene dibromide, or the brominated compound corresponding to Dutch liquid, may be procured by placing bromine in a flask and transmitting into it a current of olefiant gas as fast as it is absorbed; a rapid combination occurs, the temperature rising sensibly. The bromine is gradually decolorized, and an ethereal liquid of aromatic odour, and a pungent but sweet taste, is obtained. It may be purified by agitating it with caustic potash, then distilling from oil of vitriol and subsequently from caustic baryta.

(490) *Ethylene diniodide*, or *Glycol diniodide* [ $(C_2H_4I_2 = 282)$ ; *Sp. Gr.* 2.07; *Fusing-pt.*  $163^\circ.4$  ( $73^\circ C.$ )], or the compound of olefiant gas with iodine corresponding to Dutch liquid, is a solid which crystallizes in long, colourless, silky needles, or in flexible plates: it has a sweetish taste and an ethereal penetrating odour, which causes headache; it melts at  $163^\circ$ , and forms a crystalline mass on cooling. It may be sublimed in a current of olefiant gas, but cannot be sublimed in air or *in vacuo* without being decomposed; it slowly undergoes spontaneous decomposition, becoming brown at ordinary temperatures, especially under the influence of light. This compound may be obtained by placing iodine in a flask with a long neck, heating it by means of a water-bath to  $131^\circ$  or  $140^\circ$  ( $55^\circ$  or  $60^\circ C.$ ), and transmitting a current of olefiant gas. The iodine melts and absorbs the gas, whilst the new compound as it is formed undergoes partial sublimation. It is also said to be obtained by decomposing ethyl iodide by transmission through a porcelain tube heated to redness. It may be purified by washing with a weak solution of potash and recrystallization from boiling alcohol.

(491) **LIGHT CARBURETTED HYDROGEN: Subcarburetted Hydrogen; Methyl Hydride; Marsh Gas** ( $CH_4 = 16$ ); *Theoretic Sp. Gr.* 0.5528; *Observed*, 0.5576; *Mol. Vol.*  ; *Rel. wt.* 8.

*Preparation.*—1.—This gas is best obtained in a state of purity by a process recommended by Persoz:  $10\frac{3}{4}$  parts of the baric hydrate and  $10\frac{1}{2}$  of anhydrous sodic acetate are very intimately mixed, and heated over a charcoal fire in a Florence flask, coated with a luting of fire-clay made into a paste with a solution of borax. The flask is fitted with a cork and bent tube, and the gas is collected over water in the usual way.\* A mixture of 2 parts of caustic potash and 3 of quicklime may be substituted for the baric hydrate.

2.—The gas is also easily procured (mingled with nitrogen and carbonic anhydride), as a result of the decomposition of vegetable matter contained in the mud of stagnant pools; and hence its name of *marsh gas*. In order to collect the gas from this



source a bottle may be filled with water, inverted in the pool, and having fastened a funnel in the neck of the bottle, the mud beneath is stirred with a stick; the gas then rises into the bottle in bubbles.

3.—Light carburetted hydrogen is one of the usual products of the destructive distillation of organic substances, such as wood, peat, and bituminous coal, and it is one of the principal constituents of coal-gas; it also occurs abundantly in many coal mines, bursting forth unexpectedly from the seams of coal, and blowing out from the fissure for many months together, as though escaping from under high pressure. These natural discharges of the gas the miners term 'blowers.' According to the experiments of Graham, the gas from the Newcastle coal-field is free from admixture with olefiant gas, hydrogen, carbonic oxide, and carbonic anhydride.

*Properties.*—Marsh gas is a colourless, inodorous, and tasteless gas, scarcely soluble in water, but soluble in alcohol to a small extent: not injurious to life if diluted with air. It does not support combustion, but it is itself inflammable, and burns with a yellow luminous flame. By passing through it a continued succession of electric sparks, or by sending it through tubes heated to whiteness, it is decomposed; its carbon is deposited, and a volume of hydrogen, double that of the gas employed, is set at liberty. Chlorine has no effect upon it in the dark, but if the two gases be mixed and exposed in a moist condition to diffused light, hydrochloric acid and carbonic anhydride are formed;  $\text{CH}_4 + 4\text{Cl}_2 + 2\text{H}_2\text{O} = \text{CO}_2 + 8\text{HCl}$ . An excess of chlorine converts marsh gas into hydrochloric acid and carbonic tetrachloride ( $\text{CCl}_4$ ), when the mixture is exposed to light.

Marsh gas requires twice its volume of oxygen for complete combustion. The 3 volumes of the mixed gases after detonation, are condensed into 1 volume; they yield 1 volume of carbonic anhydride, and 2 volumes of steam which are immediately condensed. Now carbonic anhydride contains its own bulk of oxygen; it therefore represents one of the 2 volumes of oxygen which have disappeared, whilst the other volume of oxygen has united with 2 volumes of hydrogen and formed water. Light carburetted hydrogen must consequently contain twice its volume of hydrogen, condensed with its own volume of carbon vapour into the space of 1 volume, and its composition may be thus represented:—

			By weight.		By vol.	Sp. gr.
Carbon ...	... C	=	12 or 75	2 ? or 1 ?	=	0·4146
Hydrogen ...	... H <sub>4</sub>	=	4 25	4 2	=	0·1382
Marsh gas	... CH <sub>4</sub>	=	16 100	2 1	=	0·5528

When marsh gas is mixed with air, an explosive mixture is formed, termed by the miners *fire-damp*, which takes fire on the approach of a light, and often occasions accidents attended with loss of life to those who are engaged in coal mines. The fatal results of an explosion of fire-damp in the mine are not, however, limited to the mechanical violence which it occasions to the sufferers. The 'after-damp,' as the miners term it, or vitiated atmosphere that the explosion produces, is often fatal to those employed in other parts of the mine, or to the generous but ignorant and rash survivor who attempts to descend into the pit before it has been properly ventilated, in order to succour his comrades, or to ascertain their fate. From the composition of marsh gas it is obvious that this gas in exploding renders ten times its bulk of atmospheric air unfit for respiration; the 2 volumes of oxygen which 10 volumes of air contain, producing 1 volume of carbonic anhydride, and 2 volumes of steam which become condensed, leaving 8 volumes of nitrogen at liberty.

It was with a view of discovering some means of preventing these fatal results that Davy instituted those important researches on flame which led him to the invention of the *safety-lamp*, an instrument which has prevented many serious accidents, and has enabled many coal-fields to be worked which otherwise must have been abandoned, on account of the abundant escape of carburetted hydrogen from the workings.

(492) *Principle of the Safety Lamp*.—The temperature required for the combustion of different bodies varies greatly: some take fire at a very low temperature,—phosphorus, for instance, at the heat of the body; carbonic disulphide at about  $419^{\circ}$  ( $215^{\circ}$  C.); sulphur at about  $482^{\circ}$  ( $250^{\circ}$  C.); others, as olefiant gas and hydrosulphuric acid, need a red heat. A high temperature is, however, essential to the existence of flames, and particularly of flames produced by the combustion of the hydrocarbons. Marsh gas, although inflammable, requires a much higher temperature to ignite it than most other inflammable bodies; it will not explode when mixed either with less than 3 times its bulk of atmospheric air, or with more than 18 times its volume; the gas in the latter case burns only in immediate contact with the flame of the lamp, for the large volume of air with which it is mixed prevents the temperature from rising to the point necessary for the general conflagration of the gas: the most powerful explosion is occasioned when the gas is mixed with 7 or 8 times its bulk of air.

Combustion may often be carried on below the point of in-

flammation. The smouldering wick of a taper recently blown out affords a case in point. Again, if a glowing coil of platinum wire, or a hot slip of platinum foil, be suspended in a current of coal-gas mixed with atmospheric air, the metal will be maintained at a red heat by the rapid combination of the oxygen with the gas, which, however, does not take fire until the platinum becomes heated nearly to whiteness.

Davy found that no explosion could be produced in a mixture of air and marsh gas, through a narrow tube, owing to the cooling influence which the tube exerted upon the gas; and the narrower the tube, the shorter was the length required to produce this protective effect. Hemming's safety tube for the oxyhydrogen blowpipe (347) depends for its efficacy upon the cooling influence which the metallic tubes or channels, formed by the interstices between the wires, exert upon the burning jet of gas; the heat of the flame is in this way prevented from passing backwards and causing the explosion of the mixed gases in the reservoir.

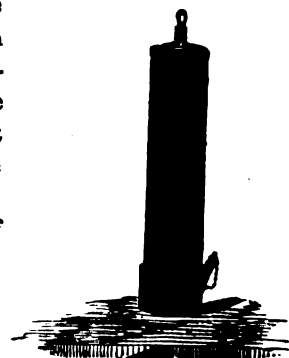
If a stout copper wire be introduced into any flame, a dark space will be observed immediately around the wire, owing to the cooling effect of the metal; a second wire cools the flame still further; and a small flame may be completely extinguished by the reduction of temperature produced by bringing down a coil of wire upon it; but if the same coil be previously heated to redness, and, whilst still hot, be placed over the flame, the latter will continue to burn.

By using wire gauze we may easily cut off the upper part of a flame, the unburned gases being cooled by its means below the point of inflammation: if a piece of gauze with large meshes be employed it will cut off the flame so long as it remains cold, but the flame will traverse the network as soon as the wire becomes red hot: with finer meshes (about 64 to the square centimetre, or 400 to the square inch) the conducting power of the metal is sufficient to cool the flame below the point of ignition, even though the wire itself be red hot. In a similar manner the gas above the gauze may be kindled, and the flame will not pass through to the gas below. Advantage is taken of this circumstance in the laboratory to obtain a smokeless flame by the use of ordinary coal-gas:—A metallic chimney, five or six inches (12 or 15 centim.) long, open below, and furnished at top with a cap of wire gauze, is placed over any convenient form of burner; the air enters at the bottom and mixes with the gas: this mixture burns above the wire gauze with a blue flame, which emits scarcely any light, and deposits no smoke upon cold objects,

provided that the supply of gas be duly proportioned to that of the air which mixes with it.\*

These principles were beautifully applied by Davy in the construction of his miner's lamp, which is merely an oil lamp (fig. 324) inclosed within a cylinder of fine wire gauze, provided with a double top, and with a crooked wire, w, which passes up tightly through a tube traversing the body of the lamp, for the purpose of trimming the wick without the necessity for removing the wire covering. When such a lamp is introduced into an explosive atmosphere of fire-damp, the flame is seen to enlarge gradually as the proportion of carburetted hydrogen increases, until at length it fills the entire gauze cylinder; when the gas is in sufficient excess the lamp is entirely extinguished; if it be withdrawn from the explosive mixture while the cylinder appears to be full of flame, the wick is generally rekindled, and the lamp continues to burn in air as usual. Whenever this pale, enlarged flame is seen, the miner must withdraw; for though no explosion can occur while the gauze is sound, yet at that high temperature the metal becomes rapidly oxidized, and might easily break into holes; a single aperture of sufficient size would then determine the fatal explosion.

FIG. 324.



The wire gauze used in the construction of these lamps contains about 121 meshes per square centimetre, or from 700 to 800 meshes in the square inch. In a strong current of air the heated gas may be blown through the apertures of the gauze before its temperature is sufficiently reduced to prevent the explosion, but such an occurrence may be easily guarded against by the use of a screen.

(493) *Nature of Flame.*—It is necessary to the production of flame, that the combustible be of such a nature as to be convertible into vapour before it undergoes combustion, otherwise no flame is produced. Well-burned charcoal or diamond burns with

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\* Bunsen's burner acts upon a similar principle. It consists of a small jet for the issue of the gas: this jet is fitted tightly into the bottom of a brass tube, which for the poor gas burned in London may be 4 or 5 inches (10 or 12<sup>cm.</sup>) long, and  $\frac{5}{16}$ ths of an inch (16<sup>mm.</sup>) in diameter. The air enters by holes in the sides of the tube near the bottom, and the mixture of gas and air is kindled at the top of the tube.

a steady glow, unattended with flame, as also does iron wire. None of these substances are susceptible of volatilization at the temperature attending their combustion. Sulphur, phosphorus, and zinc pass into the *aëriform* condition before they attain a temperature as high as that generated by their combination with oxygen, and they, as well as the various combustible gases, burn with flame.

Flame is, in fact, produced whenever a continuous supply of combustible vapour or gas is made to combine at a sufficiently elevated temperature with atmospheric oxygen, or with some gaseous supporter of combustion. In all ordinary cases, therefore, flame is a luminous envelope which forms a limiting surface between the unburned combustible within and the supporter of combustion without. This hollow structure of flame may be easily shown by experiment. If a wooden match be held for a few seconds across the middle of the flame of a spirit-lamp with a large wick, the match will become charred at the edges of the flame, but the intermediate portion will remain uninjured. If a fragment of phosphorus be placed in a small deflagrating spoon, ignited, and then introduced into the middle of the flame, it will be extinguished; but it will burn with its former energy the moment that the spoon is withdrawn from the flame. The tapering form which flames assume, is due to the ascending current produced in the atmosphere by the heat attendant on the combustion. Within the burning portion of the flame is an atmosphere of unburned combustible matter; by inserting into a flame such as that of a wax candle, just above the wick, the lower extremity of a glass tube, open at both ends, about  $\frac{1}{4}$  of an inch or 8 millimetres in diameter, and five or six inches (12 or 15 centimetres) long, the gases in the interior may be drawn off, and may be ignited at the upper aperture of the tube.

It is important to remark that the light and the heat emitted by flames are by no means proportioned to each other. The heat is due solely to the energy of the chemical action; and when a pure gaseous matter, without solid particles, composes both the burning body and the product of the combustion, little or no light is emitted:—for this reason the flame of a jet of hydrogen is barely visible in clear daylight; and that of the oxyhydrogen jet itself, although one of the most intense sources of heat at our command, is scarcely more luminous than the flame of hydrogen. For the same reason the light of sulphur burning in oxygen is feeble, notwithstanding the intense energy with which they combine: both the vapour of sulphur and sulphurous anhydride are

gaseous bodies. Phosphorus and chlorine, though they unite so energetically as to take fire at ordinary temperatures by mere contact, yet emit but little light during their combustion: the chlorides of phosphorus, as well as phosphorus itself, being very volatile bodies.

It is generally stated that in all luminous flames the light is emitted from solid particles highly ignited. The light from bodies feebly ignited is red; as the temperature rises the light becomes yellow, then white, and when the heat is very intense, the more refrangible rays of the spectrum predominate, so that it has a shade of blue or violet (89). A flame which in ordinary circumstances gives but little light may at a higher temperature become luminous, as is seen when a mixture of chlorine and hydrogen, or of oxygen and hydrogen is fired under pressure, as in the Cavendish eudiometer; although it is but feebly luminous when a jet of the mixed gas is burned, at a lower temperature, as in air.

By introducing a solid object into a feebly luminous flame, a platinum wire, for example, into the oxyhydrogen jet, or, better still, a body which, like lime, does not melt at that temperature, the light becomes so intense that the eye can scarcely support it. Such bodies, however, since they do not contribute to the chemical changes occurring in the flame, necessarily reduce its heat, owing to their conducting power. It is immaterial whether the bodies so introduced be combustible, or have already undergone perfect combustion:—the flame of hydrogen may be rendered luminous either by blowing a little powdered charcoal through it, or by allowing finely powdered magnesia, zincic oxide, or the white fumes of phosphoric anhydride produced by the combustion of phosphorus, to traverse it. Indeed no better illustration of this point can be given than is afforded by contrasting the painfully intense light produced by the combustion of phosphorus in oxygen, where the solid scarcely volatile phosphoric anhydride is produced, with the feeble light emitted by the same body as it burns in chlorine. Still, as Frankland remarks, there are cases where light of considerable intensity is emitted where no solid particles are formed during combustion. Arsenicum, when burned in a current of oxygen, emits a sensible amount of light, although the arsenious anhydride produced is vaporized below a red heat, and sulphide of arsenic (realgar), when mixed with a suitable proportion of nitre, furnishes so intense a white light that it is used as a signal light under the name of Indian fire. In the last case, however, solid particles are produced by the combustion, which furnishes potassic sulphate among the products.

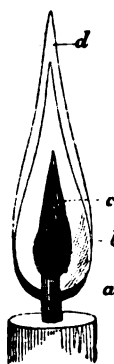


In like manner Frankland urges that carbonic disulphide, when burned in air, furnishes a pale lambent blue flame without any sensible light, but if mixed with oxygen it forms on explosion an intense white light, and if nitric oxide be substituted for oxygen, a similar intense flash of light accompanies the rapid combustion and high temperature which ensue; but it is not impossible that in this case also a separation of solid particles of carbon may occur at the moment of ignition.

The flames used for illuminating purposes are all produced by the combustion of compounds of carbon and hydrogen. All of them, notwithstanding the perfect transparency of the gas before combustion, contain solid particles of carbon during the act of combustion. The separation of carbon during the process of combustion may be proved by the simple expedient of introducing a cold body, such as a plate of metal, or a piece of glass, into a luminous flame; it becomes speedily blackened from the deposition of carbon.

The flame of a candle is sustained by the decomposition of the melted wax or tallow absorbed by the wick, and its conversion into gaseous hydrocarbons by the heat of the combustion. At the lower part of the flame, *a*, fig. 325, these hydrocarbons are immediately mingled with atmospheric air, no separation of carbon occurs here, and they burn with a pale blue light. The greater portion of the combustible gases and vapours, however, is still unburned; these vapours rise above the wick, forming the central dark part *c*, of the flame: here they are subjected to a high temperature from the combustion of the blue portion already mentioned; the heat now causes the separation of the carbon in the solid form, which becomes intensely ignited in the burning gas, emitting light in the part marked *b*; and this carbon itself, in a properly adjusted flame, gradually burns away without residue or smoke, as it comes to the surface, *d*, and meets with oxygen.

FIG. 325.



In order to produce the maximum amount of light, the point which requires the greatest attention is the due adjustment of the supply of air; if too much be given, the gas burns with a blue, feebly luminous flame; an effect which may be seen by blowing upon a common gas flame, or by watching the effects of the wind upon the exposed gaslights at night: the lengthening of the chimney of a lamp produces a similar effect. In these cases the gas becomes immediately mixed with the oxygen of the air,

and it is completely burned before it has been exposed to an elevated temperature for a time sufficiently long to allow of the separation of carbon. Moreover, it is cooled by contact with portions of the air which do not participate in the chemical action. The supply of air, however, must not be too much limited; otherwise, as may be seen by closing the central tube which admits air to an argand burner, the light becomes red from the reduction of temperature, the carbon passes off unburned, and the oxygen being insufficient to complete the combustion, the flame becomes smoky. The light of a flame is increased by any contrivance which, without deranging the order of the combustion, concentrates it into a smaller space, so as to raise the temperature of the deposited carbon to the maximum; whilst the velocity of the current of air is moderate, so as to prolong as much as possible the time during which the particles are maintained in the ignited state. It is in this way that an argand burner produces a far greater amount of light with a given consumption of gas, than if the same quantity of gas were burned in separate jets.

Frankland (*Phil. Trans.* 1861, 631) found that the rate at which candles and other similar combustibles burn, is not altered by variations in the atmospheric pressure. Candles burned at the top of Mont Blanc at the same rate as in the valley of Chamonix; but the luminosity of the flame is greatly affected by the pressure, for the amount of light emitted by the same candle on the summit of Mont Blanc was far less than that which it produced in the valley; and by careful experiments conducted under regulated pressures, it was found that as the pressures decreased from 30 to 14 inches (760<sup>mm.</sup> to 353<sup>mm.</sup>) of mercury, the illuminating power gradually diminished. In a series of experiments upon the light of burning gas, Frankland found that taking the light emitted by the combustion of a given volume of gas, in a certain burner, under the ordinary pressure of 30 inches (or 760<sup>mm.</sup>) of mercury, at 100, the same volume of gas for each diminution of 1 inch in the pressure gave 5·1 less light; the diminution of light being directly as the diminution of pressure: so that at 14 inches (353<sup>mm.</sup>) the light emitted instead of amounting to 100 was reduced to 18·4; and this rate of diminution was found to hold good with the light of hydrocarbon flames generally.

On the other hand, the luminosity of all flames may be proportionately increased by augmenting the atmospheric pressure. So rapidly does this effect increase, that an ordinary spirit-lamp which burns in the open air with scarcely any measurable

amount of light, and without smoke, becomes powerfully luminous in air at a pressure of 4 atmospheres, and when supplied with air compressed still more, even burns with a smoky flame. The result of these and other carefully devised experiments led to the unexpected conclusion that the combustion of gaseous matter is rendered less perfect in proportion as the density of the atmosphere is increased; and on the other hand, within certain limits, the more rarefied the atmosphere in which flame burns, the more complete is its combustion. No reduction in the temperature of the flame is produced by a reduction of the pressure of the surrounding air within certain limits, the observation holding good as low as 14 inches (355<sup>mm</sup>) of mercury. The decrease in illuminating power in a rarefied atmosphere is attributed by Frankland, and with strong probability, to the great readiness with which the oxygen of the atmosphere finds access to the interior of the flame, owing to the greater mobility of the particles of the air under diminished pressure.

(494) *Theory of the Blowpipe*.—The temperature of a flame may be very materially increased by augmenting the activity of the combustion, and concentrating its effect by diminishing the extent of surface over which it would otherwise take place. It is upon this principle that all blowpipes act: a jet of air or of oxygen is thrown into the interior of a flame; the combustion is thus rendered more rapid, it is limited to a much smaller space, and is entirely changed in character.

The mouth-blowpipe is one of the most valuable and portable instruments of research which the chemist possesses: he is enabled by its means, in a few minutes, to arrive with certainty and economy at results which without its aid would require much expenditure both of fuel and of time; and it often affords information which could be obtained in no other way.

FIG. 326.



The mouth-blowpipe consists essentially of a bent tube, terminating in a fine uniform jet, with a chamber for the condensation of moisture from the breath. A very convenient form of the instrument is shown at fig. 326. It consists of a conical tube of tin plate, about 8 inches (20 cm.) long, open at the narrow end, *a*, which is rounded off so as to adapt itself to the lips, and closed at its lower end, from the side of which projects a brass tube, *b*, about an inch (25<sup>mm</sup>) in length, upon which is fitted a small brass jet. This jet is inserted to a short depth into the flame of a candle,

about an eighth of an inch, or  $3^{\text{mm}}$ , above the wick as at *B* : when a current of air from the blowpipe is directed horizontally along the surface of the wick, the

FIG. 327.

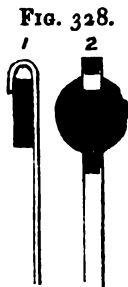


flame loses its luminosity, and is projected laterally in the form of a beautiful pointed cone, in which three parts are distinctly discernible (see fig. 327). In the centre is a well-defined blue cone; outside that is the brilliant part of the flame, terminating at *a*, and exterior to that is a pale yellow flame, *c*. The different parts of this flame possess very different properties. The blue cone is formed by the admixture of air with the combustible gases rising from the wick, and it corresponds to the blue portion, *a*, of an ordinary flame, fig. 325. In this part of the flame combustion is complete, and the oxygen introduced by the jet is in excess: the points where the excess of oxygen is absorbed by combination with fresh portions of the combustible vapours which are constantly rising from other parts of the wick, are clearly defined by the surface which seems to limit the blue cone. In front of this blue cone is the luminous portion, containing unburnt combustible gases at a high temperature, which of course have a powerful tendency to combine with oxygen.

If a fragment of some metallic oxide, such as cupric oxide, sufficiently small to be completely enveloped by the luminous portion, be introduced into this part of the flame, the oxide will be deprived of oxygen, in consequence of the superior attraction of the hot gases for this element, and the oxide will be reduced to the metallic state: hence this portion is termed the *reducing flame* of the blowpipe. At the apex, *c*, of the flame, the effects are reversed. Here, atmospheric oxygen at a high temperature is mechanically carried forward along with the completely formed products of combustion, and a fragment of any readily oxidizable metal, such as lead, copper, or tin, if placed at this point will quickly become coated with oxide; and hence this spot is termed the *oxidating flame* of the blowpipe. A good illustration of the opposite actions of these contiguous portions of the flame is afforded by the effects which they respectively produce on a piece of flint-glass tubing. The plumbic silicate contained in the glass is partially decomposed in the reducing flame, and the glass at this point becomes black and opaque from the reduction of the compound of lead to the metallic state; but by placing the blackened part for a few seconds in the oxidating flame, oxygen

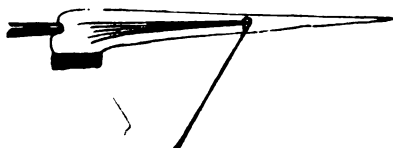
is again absorbed by the metal, and the transparency of the glass is restored.

(495) *Use of the Mouth-Blowpipe.*—The art of maintaining a continual blast by the mouth-blowpipe is not easily described, but it can be acquired by practice without much difficulty. When a substance is to be examined by the blowpipe, it may be first heated alone in a small glass tube, in order to observe whether it melts or decrepitates, or is volatilized wholly or partially. It may next be heated in a narrow tube open at both ends, to ascertain whether it burns, or changes colour, or emits any odour. It should then be ascertained whether it is reduced to the metallic state, and if it be reduced, what is the colour of the metal; whether it fuses easily, or whether it is brittle, crystalline, or malleable. These observations upon reduction may be best made when the globule is exposed to the flame upon a disk of charcoal, which may be conveniently supported, as proposed by Mr. Griffin, in the manner shown at 1, fig. 328, which represents an edge view of a slip of tin plate, about 8 inches ( $20^{\text{cm.}}$ ) long, and half an inch ( $12^{\text{mm.}}$ ) wide, bent at one end so as to hold the charcoal disk. No. 2 shows it in front. The charcoal should be sawn into slices about the third of an inch, or  $8^{\text{mm.}}$ , in thickness, so as to present a surface across the grain. A small cavity should be formed upon the upper surface of each disk for the reception of the fragment of material under examination, which should be about the size of a pin's head, or a grain of mustard-seed.



Sometimes when the substance is not easily reducible, a platinum wire bent

FIG. 329.



into a hook at one extremity forms a more convenient support, as shown at fig. 329. It may by this means be ascertained whether the substance imparts any colour to the flame; whether the body, if it be fusible, yields a transparent, an opaque, or a coloured bead; whether any change

be produced in the substance, according as it is heated in the reducing or in the oxidating flame.

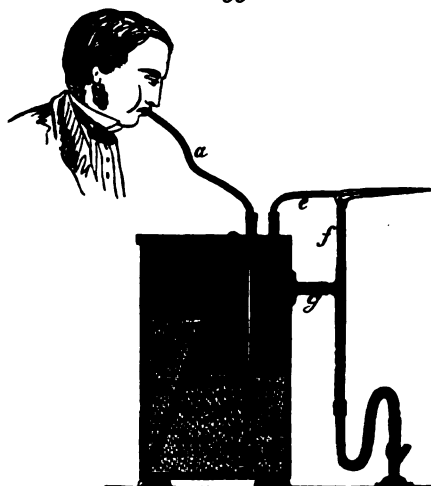
The employment of certain fluxes often aids the judgment of the operator by the colour or appearance thus produced. The most important of these fluxes are borax (592), microcosmic salt (621), and sodic carbonate, or *soda*, as it is usually simply termed in speaking of blowpipe reactions. When either borax or microcosmic salt is used, a platinum wire forms the best support; but when sodic carbonate is employed, especially for the purpose of reducing the metals, a support of charcoal is required.

Different forms of the blowpipe have been proposed, according to the purposes for which the instrument is destined. The glass-worker usually requires a large supply of air to be maintained uninterruptedly for long periods, and he commonly employs a pair of double bellows, worked by the foot.

A portable blowpipe for glass-working may be made as follows:—A rectangular box of zinc, fig. 330, about 14 inches ( $36^{\text{cm.}}$ ) high, and 6 inches (or  $15^{\text{cm.}}$ ) wide, is divided into two chambers, *c* and *d*, by a diaphragm which passes obliquely nearly to the bottom of the box; these chambers communicate with each other below; one of them, *d*, is open above, and is covered with a loose lid; the other chamber, *c*, is closed at the top: a blowpipe jet, *e*, passes just through the covering of this chamber, which is further supplied with a longer pipe, *a b*, passing

down to within a short distance of the bottom, covered with a flap of silk to prevent the return of the water in case the operator should suddenly cease to blow through *a*. If the box be now partially filled with water, the pressure of the column of liquid will expel the air through the jet, *e*, in any desired direction. By blowing down the long pipe, the operator can renew the supply of air as often as may be necessary; it bubbles up into the closed chamber, *c*, driving the water back into the open one, when the column of liquid, by its pressure, renews the blast as before. The gas-burner, *f*, can be raised or lowered as may be necessary, and by means of a sliding joint, *g*, can be made to approach towards or recede from the jet, *e*, as may be required. An oil-lamp may be used when gas is not at hand; it has, indeed, the advantage of giving a more intense heat than gas, and it is less likely to reduce the oxide of lead contained in flint glass.

FIG. 330.



Where a very intense heat is required, a spirit-lamp, or gas-flame, through which a current of oxygen from a gas-holder is directed, may be employed; and occasionally, in cases where a still stronger heat is requisite, recourse may be had to the oxyhydrogen blowpipe, in which, owing to the complete intermixture of the two gases, the flame is solid, and therefore of small dimensions.

(496) OIL-GAS, *Tetrylene* or *Butylene* ( $C_4H_8 = 56$ ); *Rel. wt.* 28; *Sp. Gr. of Gas*, 1.854; *of Liquid at 53° 6 (12° C.)*, 0.627; *Mol. Vol.*  .—This compound was discovered by Faraday to be one of the constituents of the gases obtained by the destructive distillation of oil. It is almost insoluble in water, but is taken up freely by alcohol, and still more abundantly by oil of vitriol. Oil-gas is condensed at  $0^\circ$  ( $-4^\circ$  C.) to a colourless liquid; the gas itself is colourless, and burns with a white, powerfully luminous flame. It contains the same proportions of carbon and hydrogen as olefiant gas, but the two elements are condensed in oil-gas into half the bulk which they occupy in olefiant gas. One volume of this gas requires 6 times its bulk of oxygen for its complete combustion, 4 volumes of steam and 4 volumes of carbonic anhydride being the products. Consequently its composition may be thus represented:—

	By weight.		By vol.		Sp. gr.
Carbon	$C_4 = 48$	or 85.71	8 p	or 4 p	= 1.658
Hydrogen	$H_8 = 8$	14.29	8	4	= 0.276
Oil gas	$C_4H_8 = 56$	100.00	2	1	1.934

### § III. COMPOUNDS OF CARBON WITH OXYGEN.

(497) Besides carbonic oxide and carbonic anhydride, carbon forms several other oxides, which are not known in the separate form, but which, when united with the elements of water, possess acid characters: viz.,

Oxalic acid . . . .	$\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$	=	90 + 36
Rhodizonic acid . . . .	$\text{H}_3\text{C}_3\text{HO}_6$	=	160
Croconic acid . . . .	$\text{H}_2\text{C}_3\text{O}_6, 3\text{H}_2\text{O}$	=	142 + 54
Mellitic acid . . . .	$\text{H}_2\text{C}_6\text{O}_4$	=	114

(498) OXALIC ACID; *Dihydric oxalate* ( $\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O} = 90 + 36$ ); *Sp. Gr.* 1.64.—This important and powerful acid may be usefully introduced here, though it belongs to the division of organic chemistry, as it is always obtained from sugar, starch, or some other substance of organic origin, and is one of the products of the oxidation of these substances under the influence of hot nitric acid or of potassic hydrate; it is moreover a frequent constituent of the juices of plants. Oxalic acid is abundant in the leaves of the wood-sorrel (*Oxalis acetosella*), to which it communicates their powerfully acid taste, and in which it occurs in combination with potassium as the salt commonly known as binoxalate of potash. It is found likewise in the *Rumex acetosa* and in the leaf-stalks of the common rhubarb. Many lichens owe their solidity to the presence of calcic oxalate, and have been employed as a source of the acid. It is also contained abundantly in the barilla plant, in the form of neutral or disodic oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ ).

*Preparation.*—Oxalic acid may be procured by heating tartaric, citric, or malic acid with an excess of potassic hydrate; and when starch, sugar, or ligneous tissue is similarly treated, hydrogen is evolved and potassic oxalate is among the products. Many tons of oxalic acid are indeed now made weekly for the calico-printer by heating sawdust with a mixture of potassic hydrate.

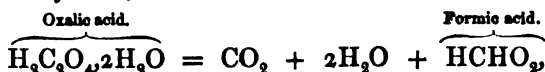
The following is the method (Schunck, Smith, and Roscoe, *Brit. Assoc. Report*, 1861, p. 120) employed by Messrs. Roberts, Dale, and Co., for manufacturing oxalic acid from sawdust on a large scale. A concentrated solution of mixed caustic soda and potash (sp. gr. 1.35) is prepared, containing 2 atoms of sodic hydrate to 1 atom of potassic hydrate. Caustic soda alone does not furnish oxalic acid by this method, and caustic potash singly is too expensive; hence a mixture of the two is necessary. Sawdust is introduced so as to form a stiff paste. The pasty mass is placed in thick layers upon heated iron plates, and stirred constantly whilst the temperature is gradually raised. At first water escapes freely; as the decomposition advances the mass swells up and disengages an inflammable gas, containing hydrogen and carburetted hydrogen, accompanied with an aromatic odour. The temperature is maintained at a point between  $392^\circ$  and  $482^\circ$  ( $200^\circ$  and  $250^\circ$  C.), for a couple of hours, when a dark brown mass, wholly soluble in water, is obtained. The exact nature of this mixture is not ascertained. At present, however, it contains only from one to four per cent. of oxalic acid, and a trace of formic, but no acetic acid; the application of heat to the mass is therefore continued for 3 or 4 hours longer, taking care to avoid charring. The mass becomes thoroughly dry, and finally contains from 28 to 30 per cent. of oxalic acid; hydrogen appears to be given off continuously during the process, which is quite successful in closed vessels.

The grey mass thus procured is treated with water at  $59^{\circ}$  ( $15^{\circ}$  C.), which dissolves out everything but the sparingly soluble sodic oxalate. The mother-liquors after the separation of the sodic oxalate are boiled down to dryness, ignited to destroy organic matter, and the alkalies are again rendered caustic, and after the addition of a suitable quantity of soda, are used in preparing a fresh charge.

The sodic oxalate is decomposed by boiling with hydrate of lime, calcic oxalate is formed, and separates in the insoluble condition, whilst caustic soda enters into the solution, and may be used over again. Meantime the calcic oxalate is decomposed by means of sulphuric acid, and the liquor decanted from the calcic sulphate furnishes crystals of oxalic acid on evaporation. Sawdust treated by this method yields about half its weight of crystallized oxalic acid.

But the acid is still commonly prepared by the older plan of oxidation of sugar or of starch by nitric acid :—1 part of dry loaf sugar is dissolved in  $8\frac{1}{2}$  parts of nitric acid, of sp. gr. 1.38, and heated in a flask until all effervescence has ceased; a copious evolution of carbonic anhydride and of nitric oxide attends the reaction. The solution is then evaporated by a water-bath to one-sixth of its bulk, and the acid crystallizes on cooling. The mother-liquor may be further concentrated by evaporation: the oxalic acid is purified by recrystallization, and amounts to more than half the weight of the sugar employed (Schlesinger). Starch may be substituted for the sugar in this process, with results nearly as good.

*Properties.*—Oxalic acid as thus obtained crystallizes in transparent four-sided prisms, which are represented by the formula ( $\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$ ). This acid requires about 9 times its weight of cold water for solution, but it is dissolved much more freely by boiling water; it is also soluble in alcohol. The crystals when heated suddenly to  $212^{\circ}$  ( $100^{\circ}$  C.) melt in their water of crystallization; but if slowly raised to  $212^{\circ}$  they become opaque, and lose 28.5 per cent. of water. The residue then consists of  $\text{H}_2\text{C}_2\text{O}_4$ . If these dried crystals be placed in a retort, and heated by means of an oil-bath to between  $302^{\circ}$  and  $320^{\circ}$  ( $150^{\circ}$  and  $160^{\circ}$  C.), they are slowly sublimed and may be condensed in white needles; but if heated above  $320^{\circ}$  ( $160^{\circ}$  C.) the acid is decomposed. When the crystallized oxalic acid is heated quickly without previous desiccation, it melts in its water of crystallization, and at  $311^{\circ}$  ( $155^{\circ}$  C.) is resolved, with apparent ebullition, into a mixture of carbonic anhydride, formic acid, water, and carbonic oxide :—



the carbonic oxide is derived from the formic acid, which when decomposed by heat yields carbonic oxide and water;  $\text{HCHO}_2$  becoming  $\text{H}_2\text{O} + \text{CO}$ . Berthelot has shown that the conversion



of oxalic into formic acid is easily effected by dissolving the oxalic acid in glycerin, and heating to about  $302^{\circ}$  ( $150^{\circ}$  C.), when formic acid slowly passes over, and carbonic anhydride escapes; but if the temperature be raised to  $383^{\circ}$  ( $195^{\circ}$  C.) carbonic oxide is obtained in abundance. When heated with oil of vitriol, or phosphoric anhydride, it breaks up into equal volumes of carbonic oxide and carbonic anhydride. No anhydride of oxalic acid appears to exist.

The composition of oxalic acid is as follows:—

	Unknown anhydride.		Hydrated.		Crystallized.
Carbon ...	$C_2=24$ or $33\cdot3$		$C_2=24$ or $26\cdot6$		$C_2=24$ or $19\cdot05$
Oxygen ...	$O_3=48$ $66\cdot7$		$O_3=48$ $53\cdot4$		$O_3=48$ $38\cdot10$
Water ...	— — —		$H_2O=18$ $20\cdot0$		$3H_2O=54$ $42\cdot85$
Oxalic an- hydride }	$C_2O_3=72$ $100\cdot0$		$H_2C_2O_4=90$ $100\cdot0$		$H_2C_2O_4\cdot 2H_2O=126$ $100\cdot00$

The solution of oxalic acid has an intensely sour taste; if swallowed, the acid acts as a powerful poison, occasioning death in a very few hours. The best antidote in such a case is the administration of chalk or of magnesia suspended in water.

It is a general rule that when an elementary body forms two or more acids with oxygen, the acid which contains the largest amount of oxygen is the most energetic in its action. For example, the sulphuric acid is more powerful than the sulphurous; chloric acid is stronger than hypochlorous acid, and the perchloric acid is stronger than either. It is, however, otherwise in the case of oxalic acid; although oxalic acid contains a smaller proportion of oxygen than carbonic acid, its attraction for bases is much more energetic, and it decomposes all the carbonates with effervescence. It even liberates hydrochloric acid when heated with dry sodic chloride. The cause of this remarkable exception to the general rule has not hitherto been explained.

*Oxalates.*—Until lately oxalic acid was regarded as monobasic; but there are good reasons for viewing it as dibasic. Besides the two classes of salts usually formed by dibasic acids, the oxalic furnishes with the alkali-metals a group of super-acid salts, represented by the so-called quadroxalate of potash. Normal or *dipotassic oxalate* ( $K_2C_2O_4\cdot H_2O$ ) furnishes efflorescent very soluble prismatic crystals: the *hydropotassic oxalate* (or *bin-oxalate*,  $KHC_2O_4\cdot H_2O$ ) is sparingly soluble in cold water, and requires about 14 parts of boiling water for solution; it crystallizes in large prisms which are unaltered by exposure to the air; and the *quadroxalate* ( $KHC_2O_4\cdot H_2C_2O_4\cdot 2H_2O$ ) furnishes large crystals which are still less soluble. The so-called *salt of lemons* is one

of these acid oxalates. Oxalic acid forms a large number of insoluble salts. The insolubility of calcic oxalate in water has led to the employment of oxalic acid as a reagent for indicating the existence of lime in solution, and for determining its amount. On adding a neutral oxalate to a neutral or alkaline solution of any salt of calcium, calcic oxalate falls as a white precipitate, which is insoluble in acetic acid. After drying at  $104^{\circ}$  ( $40^{\circ}$  C.), this salt consists of  $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , if dried at  $212^{\circ}$ , it retains only  $\text{H}_2\text{O}$ , and when heated to bright redness, 100 parts leave 34.15 of pure quicklime, corresponding to 43.9 of oxalic anhydride. The oxalates of magnesium, cadmium, and manganese are also white and nearly insoluble: they each, when dried at  $212^{\circ}$  retain  $2\text{H}_2\text{O}$ . Zincic oxalate is white; cobalt oxalate is rose-coloured; nickel oxalate is greenish white, and ferrous oxalate is yellow: they are all sparingly soluble, and retain  $2\text{H}_2\text{O}$  at  $104^{\circ}$  ( $40^{\circ}$  C.). The oxalates of barium and strontium are white, and that of copper is of a pale blue: they are nearly insoluble, and retain  $\text{H}_2\text{O}$  at  $212^{\circ}$ . The oxalates of lead and silver are white, and anhydrous. All the insoluble oxalates are readily dissolved by diluted nitric acid.

An insoluble basic plumbic oxalate ( $\text{PbC}_2\text{O}_4 \cdot 2\text{PbO}$ ) may be obtained by precipitating the tribasic acetate of lead by means of a neutral soluble oxalate. One of the most characteristic salts of this acid is argentic oxalate, which when heated on platinum foil is suddenly reduced to the metallic state, and is dispersed with a slight explosion, owing to the sudden liberation of carbonic anhydride;  $\text{Ag}_2\text{C}_2\text{O}_4 = \text{Ag}_2 + 2\text{CO}_2$ . The oxalates of many other of the metals which have but small attraction for oxygen, those of cobalt and nickel among the number, are reduced to the metallic state if heated to redness in a closed vessel, so as to exclude atmospheric oxygen; 2 atoms of carbonic anhydride being expelled, whilst the pure metal is left behind. This reducing action occurs in the case of gold, when a solution of a salt of this metal is simply boiled with an oxalate; the gold is precipitated either in flakes or in the form of a very finely divided powder. The oxalates of the metals of the alkalies and the alkaline earths are converted by a dull red heat into carbonates of these metals; carbonic oxide burning off with a pale blue flame, whilst the salt does not exhibit any appearance of charring.

The general formulæ of the oxalates are the following—the table includes some of the principal oxalates:—

Normal oxalates	...	...	...	...	$\text{M}_2\text{C}_2\text{O}_4$
Acid oxalates	...	...	...	...	$\text{MHC}_2\text{O}_4$

Super-acid oxalates	...	...	...	...	$\text{MH}_2\text{C}_2\text{O}_4$
Dipotassic oxalate	...	...	...	...	$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$
Potassio hydric oxalate (binoxalate)	...	...	...	...	$\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
Potassio trihydric dioxalate (quadroxalate)	...	...	...	...	$\text{KH}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
Diammonic oxalate	...	...	...	...	$(\text{H}_4\text{N})_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$
Ammonio hydric oxalate (binoxalate)	...	...	...	...	$\text{H}_4\text{NHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
Baric oxalate	...	...	...	...	$\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
Strontic "	...	...	...	...	$\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
Calcic "	...	...	...	...	$\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
Magnesian "	...	...	...	...	$\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
Zincic "	...	...	...	...	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
Cadmic "	...	...	...	...	$\text{CdC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
Cobalt "	...	...	...	...	$\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
Nickel "	...	...	...	...	$\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
Ferrous "	...	...	...	...	$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
Cupric "	...	...	...	...	$\text{CuC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
Plumbic "	...	...	...	...	$\text{PbC}_2\text{O}_4$
Argentio "	...	...	...	...	$\text{Ag}_2\text{C}_2\text{O}_4$

Oxalic acid forms a large number of double salts,—such as the following :—

Uranous diammonic dioxalate  $[\text{U}''(\text{H}_4\text{N})_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}]$ .

Uranico-ammonic oxalate  $(\text{UOH}_4\text{NC}_2\text{O}_4 \cdot 2\text{H}_2\text{O})$ .

Chromico-tripotassic trioxalate  $(\text{K}_3\text{Cr}'''3\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O})$ .

(499) *Rhodizonic, Croconic, and Mellitic Acids*.—Three other acids containing carbon and oxygen are known under these names, but they are of slight importance.

*Rhodizonic Acid* ( $\text{H}_2\text{C}_2\text{HO}_4$ ; Will) is an acid which forms salts of a beautiful red or scarlet colour, whence it derives its name (from  $\rho\acute{o}\delta\omicron\nu$ , a rose). It is obtained by the action of a moist atmosphere on the dark olive-green compound which potassium yields when gently heated in carbonic oxide gas, and which is formed abundantly during the preparation of potassium.

If the aqueous solution of potassic rhodizonate ( $\text{K}_2\text{C}_2\text{H}_2\text{O}_4 \cdot \text{H}_2\text{Q}$  ?) be boiled in the presence of free alkali, it is decomposed with loss of water into the salt of a new acid, which from the yellow colour of its compounds is termed *Croconic acid*,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ .

Croconic acid is obtained by decomposing potassic croconate with silicofluoric acid. It forms yellow crystals soluble both in water and in alcohol. Croconic acid and the soluble croconates furnish yellow sparingly soluble crystalline plates when mixed with salts of barium or of lead, (Will, *Lieb. Annal.* cxviii. 187).

(500) *Mellitic Acid* ( $\text{H}_2\text{C}_6\text{O}_4$ ), has hitherto been found only in *Mellite*, a rare mineral, consisting of aluminic mellitate ( $\text{Al}_3\text{C}_6\text{O}_4 \cdot 18\text{H}_2\text{O}$ ), which is now and then met with in lignite, and occurs crystallized in honey-yellow transparent octohedra. Mellitic acid is extracted from mellite by boiling the powdered mineral with ammoniac sesquicarbonate; ammoniac mellitate is obtained in solution: by the addition of plumbic acetate to the liquid, plumbic mellitate ( $\text{PbC}_6\text{O}_4 \cdot \text{H}_2\text{O}$ ) is precipitated. This precipitate, when washed, is suspended in water and decomposed by a current of sulphuretted hydrogen; plumbic sulphide is thus formed, and is separated by filtration from the solution which contains the liberated mellitic acid: on evaporating the liquid the acid is left in a state of purity.

Mellitic acid is soluble in water and in alcohol; it may be obtained crystallized in groups of needles by the spontaneous evaporation of the alcoholic solution. Its solution reddens litmus strongly, and has a strongly sour taste. Mellitic acid is unchanged by boiling nitric or sulphuric acids. The acid is decomposed by heat into a volatile crystalline sublimate, and into carbon. With the salts of lead the mellitates give a voluminous white precipitate, which gradually shrinks in bulk and becomes crystalline.

#### § IV. COMPOUNDS OF CARBON WITH NITROGEN.

(501) CYANOGEN;  $CN$ , or  $Cy=26$ ; *Rel. wt.* 26; *Mol. Vol.*  $\square$ ; *Mol. wt.*  $Cy_2=52$ ; *Theoretic Sp. Gr.* 1.800; *Observed*, 1.8064; *Atomic Vol.*  $\square$ .—This substance is one of the most interesting compounds of carbon, and its discovery by Gay-Lussac, in 1814, formed an epoch in the history of chemical science. It was the first compound body which was distinctly proved to enter into combination with elementary substances in a manner similar to that in which the elements combine with each other. New views of chemical composition were thus originated, which have since acquired an extensive development, and have exercised a most material influence upon the theory of organic compounds in general. The name of *Cyanogen* (from *κίανος* blue, *γεννάω* to produce), is derived from the circumstance that this body forms an essential ingredient in Prussian blue. No direct union of its constituent elements can be effected. If a mixture of charcoal and potassic carbonate be heated to redness in a porcelain tube, and nitrogen be passed over it, carbonic oxide escapes abundantly, whilst cyanogen is formed and unites with the potassium, yielding potassic cyanide;  $K_2CO_3 + 4C + N_2 = 2KCN + 3CO$ . This operation takes place in the blast furnace during the smelting of iron, a notable quantity of potassic cyanide being formed near the hottest part (*note*, 745), the potassium being derived from the ashes of the coal or from the clay in the ore employed.

The compounds of ammonia in vapour if transmitted over glowing charcoal yield cyanogen still more readily, especially when potassic carbonate is also present. The oxidized compounds of nitrogen, such as the nitrates, likewise readily furnish small quantities of the compounds of cyanogen, as is frequently observed in deflagrating charcoal with nitre.

A sensitive reaction for the presence of nitrogen in organic compounds is founded upon the facility with which either potassium or sodium determines the formation of cyanogen from azotised compounds of carbon:—a small globule of potassium (or of sodium) is introduced into a narrow glass tube sealed at one end, and the metal is heated with the organic body under exami-

nation. The residue is then dissolved in water and a small quantity of a mixture of the ferrous and ferric sulphates added, then a slight excess of hydrochloric acid; a precipitate of Prussian blue is formed if nitrogen be present in the compound.

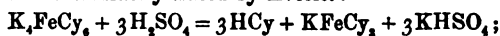
Cyanogen is also present in small quantity among the products obtained during the distillation of pit coal; and it is furnished during the decomposition of ammoniac oxalate by heat,  $2\text{H}_4\text{N}_2\text{C}_2\text{O}_4$  becoming  $(\text{CN})_2 + 4\text{H}_2\text{O}$ .

The compounds of cyanogen are, however, almost always obtained from the double cyanide of potassium and iron, a salt which crystallizes in transparent yellow tables, and is commonly known by the name of *prussiate of potash* (potassic ferrocyanide,  $\text{K}_4\text{FeCy}_6 \cdot 3\text{H}_2\text{O}$ ). This salt is prepared by heating, in a covered iron pot, about 5 parts of refuse animal matter, such as the parings of hoofs, hides, horns, &c., with 2 parts of pearlash, and iron filings; the nitrogen and carbon of the animal matters react upon each other at a high temperature, and combine with a portion of reduced potassium and with iron. On digesting the mass, when cold, with water, potassic ferrocyanide is formed, and is deposited from the solution in large four-sided tables. When 10 parts of this salt are dissolved in 4 times their weight of warm water, and distilled with 7 parts of oil of vitriol diluted with twice their weight of water, until about half the bulk of the liquid has passed over, a dilute solution of hydrocyanic acid ( $\text{HCy}$ ) is formed;\* this, if saturated with mercuric oxide, furnishes, on evaporation, a crystallizable compound, the mercuric cyanide ( $\text{HgCy}_2$ ). If this be thoroughly dried, and heated in a retort, it is decomposed into mercury, which distils over, and cyanogen, which passes off as a permanent gas.

Cyanogen is a transparent colourless gas, of a peculiar, penetrating odour: it is poisonous if respired. It burns with a beautiful rose-edged purple flame. Cyanogen is soluble in one-fourth of its bulk of water, and still more freely so in alcohol; hence it must be collected over mercury. In porcelain or glass vessels it supports a high temperature without decomposition, but if heated in iron tubes, charcoal is deposited, and a volume of nitrogen, equal to that of the cyanogen used, remains.

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\* The reaction in this case is rather less simple than might have been anticipated: it was first accurately traced by Everitt:—



half the cyanogen only is expelled as hydrocyanic acid, the other half remaining behind in the form of a white, insoluble, double cyanide of iron and potassium ( $\text{KFe}''\text{Cy}_2$ ).

The composition of cyanogen may be determined by detonation in the eudiometer with oxygen; the combustion is attended with a powerful explosion. One volume of cyanogen with 2 volumes of oxygen yields 2 of carbonic anhydride and 1 volume of nitrogen;  $(\text{CN})_2 + 2\text{O}_2 = 2\text{CO}_2 + \text{N}_2$ ; 2 volumes of carbon vapour and 1 volume of nitrogen must therefore be condensed in it into 1 volume, as is shown in the following table:—

		By weight.	By vol.	Sp. gr.
Carbon	...	C = 12 or 46·15	2? = 0·829	
Nitrogen	...	N = 14 53·85	1 = 0·971	
Cyanogen	...	CN = 26 100·00	1 = 1·800	

Cyanogen is readily reduced to the liquid state by a pressure of its own vapour equal to about 4 atmospheres. It forms a colourless, limpid liquid, of sp. gr. 0·866 at  $62^{\circ}\cdot6$  ( $17^{\circ}$  C.), which, on the removal of the pressure, rapidly but quietly resumes the gaseous state; according to Bunsen it boils at  $-5^{\circ}$  ( $-20^{\circ}\cdot7$  C.). It freezes at  $-30^{\circ}$  ( $-34^{\circ}\cdot5$  C.), and forms a transparent crystalline solid, which is nearly of the same density as the liquid.

Fig. 331 shows an easy method of liquefying cyanogen: a tube of hard glass is bent into the form of *a, b, c*. Into the limb, *a*, well-dried mercuric cyanide

FIG. 331.



is introduced; heat is applied to the cyanide at *a*; the bend, *b*, is placed in a basin containing a freezing mixture of ice and salt; as soon as the gas begins to escape, the stopcock at *c* is closed, and liquid cyanogen becomes condensed in the bend, *b*.

If potassium be heated in cyanogen it burns and combines with it, without occasioning the decomposition of the gas, forming a saline body analogous to common salt. This experiment shows the existence of the remarkable property possessed by cyanogen, of combining with metals and other bodies like an element. This peculiarity in the mode of combination of cyanogen, which has given rise to the theory of compound radicles now so extensively applied in organic chemistry, will be better traced by examining a few of the numerous compounds which cyanogen forms with the elementary bodies.

(502) HYDROCYANIC or PRUSSIC ACID; *Hydric cyanide*;

(HCy = 27); *Sp. Gr. of Vapour, Theoretic*, 0.933; *Observed*, 0.9476; *of Liquid*, 0.7058 at 44° 6 (7° C.); *Melting-pt.* 5° (-15° C.); *Boiling-pt.* 80° (26° 5 C.); *Atomic and Mol. Vol.*  ; *Rel. wt.* 13.5.—Cyanogen forms with hydrogen a highly important compound, though the two bodies cannot be made to unite directly with each other. If a current of dried sulphuretted hydrogen be transmitted through a long tube filled with mercuric cyanide until the cyanide has become blackened nearly throughout, mercuric sulphide and hydrocyanic acid are formed;  $\text{HgCy}_2 + \text{H}_2\text{S} = \text{HgS} + 2\text{HCy}$ ; but it may also be prepared by decomposing any of the cyanides with a strong acid, and subjecting them to distillation; for example, mercuric cyanide when treated with hydrochloric acid yields it readily. The most economical process is that of Wöhler: he prepares a crude potassic cyanide by fusing 8 parts of the dried potassic ferrocyanide with 3 of potassic carbonate and 1 part of charcoal. This decomposition is shown in the following equation;  $\text{K}_4\text{FeCy}_6 + \text{K}_2\text{CO}_3 + \text{C}_2 = 6\text{KC}_y + \text{Fe} + 3\text{CO}$ . The fused mass is treated with 6 times its weight of water, in a well-closed vessel; the clear liquid is decanted from the iron which it is the object of this operation to separate, and is poured into a retort: sulphuric acid, diluted with an equal weight of water, is gradually added in the proportion of 1 part of oil of vitriol to 2 parts of the cyanide. At first the distillation proceeds spontaneously from the heat developed by the admixture of the sulphuric acid with the water. In order to condense the acid, the products are made to pass through a long U-shaped tube, immersed in cold water, and filled with calcic chloride, with the exception of the first fourth of the tube, which contains fragments of the crude potassic cyanide; to the bent tube is attached a second delivering tube, which passes to the bottom of a bottle cooled with ice and salt. The calcic chloride in the syphon tube retains the moisture, and the potassic cyanide any sulphuric acid that might chance to pass over, whilst the hydrocyanic acid collects in the anhydrous state in the cooled receiver. The reaction of sulphuric acid upon potassic cyanide is very simple, being exactly analogous to its action upon sodic chloride;  $2\text{KC}_y + 2\text{H}_2\text{SO}_4 = 2\text{HCy} + 2\text{KHSO}_4$ . Anhydrous hydrocyanic acid is a colourless, transparent, and very volatile liquid; so rapidly does it evaporate, that if a drop be allowed to fall upon a glass plate, part of the acid becomes frozen by the cold produced by its own evaporation. Its vapour has an odour of peach blossoms, causing a peculiar sense of oppression, and of constriction in the fauces. Owing to its intensely poisonous character, and almost instant-

neous action in destroying life, the greatest care is requisite in conducting experiments upon this substance; the apparatus should always be arranged so that the vapours are carried away from the operator by a brisk current of air.

Hydrocyanic acid is very inflammable; it burns with a flame resembling that of cyanogen, but of a whiter colour. In conformity with its analogy with the hydrogen acids of chlorine and the other halogens, it is composed of 1 volume of hydrogen and 1 of cyanogen united without condensation. When potassium is heated in hydrocyanic acid vapour, potassic cyanide is formed, and a volume of hydrogen equal to half that of the vapour employed is liberated; chlorine and bromine decompose it immediately; hydrochloric or hydrobromic acid is produced, and if excess of the halogen be present, cyanogen chloride or bromide is formed. If 5 volumes of oxygen be mingled with 4 of hydrocyanic vapour, a mixture is obtained which detonates powerfully on transmitting the electric spark through it; 4 volumes of carbonic anhydride and 2 of nitrogen remain, and 2 volumes of steam are condensed;  $4\text{HCN} + 5\text{O}_2 = 4\text{CO}_2 + 2\text{N}_2 + 2\text{H}_2\text{O}$ . The composition of hydrocyanic acid may be calculated from the result of this experiment, and may be represented as follows:—

			By weight.	By vol.	Sp. gr.
Carbon ... ..	C	= 12	or 44'45	2	or 1'0 = 0'414
Nitrogen ... ..	N	= 14	51'85	1	0'5 = 0'485
Hydrogen ... ..	H	= 1	3'70	1	0'5 = 0'034
Hydrocyanic acid ...	HCN	= 27	100'00	2	1'0 = 0'933

When anhydrous hydrocyanic acid is mixed with its own weight of water, a contraction in bulk amounting to between 6 and 7 per cent. takes place, and at the same time a depression of several degrees of temperature occurs (Bussy and Buignet). The same effects are observed in a smaller degree if the two liquids are mixed in other proportions; but the maximum reduction of temperature occurs when equal weights of the two, corresponding to  $(2\text{HCy}, 3\text{H}_2\text{O})$  are taken. (*Annal. de Chimie*, IV. iii. 237.)

The acid properties of this compound are but feeble; it reddens litmus slightly, dissolves red oxide of mercury freely, and precipitates argentic nitrate in white flocculi ( $\text{AgCy}$ ). Potassic cyanide always has an alkaline reaction: its solution emits the odour of the acid. Pure hydrocyanic acid may be kept unchanged if excluded from light; but in diffused light it becomes decomposed, and a brown matter, consisting chiefly of paracyanogen, is formed. Pelouze has pointed out a remarkable decomposition which furnishes dilute hydrocyanic acid almost in a state of purity: 1 atom of



crystallized ammoniac formiate contains the elements of 1 atom of hydrocyanic acid and 2 atoms of water. If this salt be placed in a retort and heated, it melts at  $248^{\circ}$  ( $120^{\circ}$  C.), loses a little ammonia at  $284^{\circ}$  ( $140^{\circ}$  C.), and between  $356^{\circ}$  and  $392^{\circ}$  ( $180^{\circ}$  and  $200^{\circ}$  C.), distils over, and if the vapour be transmitted through a red-hot tube it is wholly converted into hydrocyanic acid and water;  $\text{H}_4\text{NCHO}_2 = \text{HCN} + 2\text{H}_2\text{O}$ . If equal measures of concentrated hydrocyanic and hydrochloric acids be mixed together, formic acid and ammonia are reproduced.

Hydrocyanic acid, mixed with a peculiar essential oil, is obtained by distillation from the kernels of the bitter almond, and from those of many varieties of stone fruit: it is also present in the water which is distilled off the leaves of the laurel, the peach, and some other shrubs; the juice of the tapioca plant (*Jatropha manihot*) likewise contains it, and it is also formed under various circumstances during the oxidation and decomposition of some kinds of azotised substances.

The preparation of diluted hydrocyanic acid by distillation of potassic ferrocyanide with diluted sulphuric acid has been already noticed, but as the acid is now frequently employed in medicine, it is highly important, on account of its energetic action, to be able to insure its preparation of an uniform strength. This is easily attained by the process of a former Pharmacopœia, which directs  $48\frac{1}{2}$  grains of argentic cyanide to be suspended in an ounce of water, and to be decomposed by  $39\frac{1}{2}$  grains of hydrochloric acid, decanting the clear liquid from the argentic chloride; this acid contains 2 per cent. of the anhydrous acid. The acid when dilute is less prone to decomposition than when concentrated, especially if a little free sulphuric acid be present: but it should always be excluded from the light. This acid is extremely volatile, and if a bottle containing the diluted acid be left open for a few hours it will be found to have suffered a very material reduction in strength; indeed, the mere opening and closing the bottle in dispensing the medicine always reduces its strength. When subjected to distillation a large quantity is usually lost, and the greater portion of the acid comes over in the first fourth of the distillate. What is called *Scheele's acid* varies greatly in strength, owing to the difficulty of condensing the acid vapour. It is directed to be prepared by mixing 10 parts of potassic ferrocyanide with 3.75 of oil of vitriol previously diluted with 40 parts of water, and distilling over till 10 parts are collected. It seldom contains more than 5 per cent. of the acid, and the proportion is often considerably less.

(503) *Cyanides*.—The cyanides of the alkali-metals are freely soluble in water. Many of the cyanides of the heavier metals are insoluble in water, but most of them are decomposed with evolution of hydrocyanic acid when boiled with hydrochloric acid; those of silver and mercury, when heated to redness, yield cyanogen gas. Solutions of mercurous salts with the soluble cyanides give a grey precipitate of the reduced metal; but the mercuric salts give no precipitate. Most of the cyanides which are insoluble in water may be dissolved by means of a solution of the cyanides of the metals of the alkalis, or of the alkaline earths; in such cases double cyanides are generally formed. Liebig has given a ready method for the exact determination of the strength of a solution of hydrocyanic acid, founded upon the solubility of these double cyanides:—The acid to be tested is supersaturated with a solution of caustic potash, and a standard solution of argentic nitrate (containing 1·7 gramme of nitrate in 100 cubic centim. of water) is gradually added, agitating the mixture after each addition; as soon as the precipitate is no longer redissolved, the number of divisions of nitrate added must be read off; 1·7 gramme of argentic nitrate represent 0·54 gramme of hydrocyanic acid. The presence of chlorides does not interfere with the application of the test. The reaction is the following:— $\text{AgNO}_3 + 2\text{KC}_y = \text{KNO}_3 + \text{KC}_y, \text{AgC}_y$ .

Cupric sulphate may be substituted for the argentic nitrate, if the hydrocyanic solution be rendered alkaline with ammonia instead of with potash; the reaction is complete as soon as the liquid acquires a slight blue tinge; 1·45 grm. of the crystallized sulphate represent 0·54 grm. of hydrocyanic acid.

*Tests*.—The presence of the soluble cyanides, or of hydrocyanic acid in solution, may be determined by the following tests:—

1. With argentic nitrate, a white curdy precipitate which does not blacken by exposure to light, is formed; it is nearly insoluble in cold nitric acid; when heated to redness it gives off the inflammable vapour of cyanogen.—2. If to the liquid a slight excess of potash be added, and then a mixture of ferrous and ferric sulphate, a precipitate of hydrated ferric and ferrous oxide is occasioned, which, when treated with excess of hydrochloric acid, leaves Prussian blue. The reaction, omitting the water of hydration of the oxide, may be thus represented;  $18\text{KC}_y + 2\text{Fe}_2\text{O}_3, 3\text{FeO} + 18\text{HCl} = 18\text{KCl} + 9\text{H}_2\text{O} + \text{Fe}_4, \text{Fe}_3\text{C}_y_{18}$ . This test may be modified by gently heating the suspected mixture with sulphuric acid, and suspending in the flask or retort for a few

minutes, a piece of paper moistened with a solution of potash; on dropping a weak solution of the mixed sulphates of iron upon the paper, and immersing it in diluted sulphuric acid, hydrocyanic acid may be recognized by the formation of Prussian blue when very minute traces only are present.—3. Let the liquid be acidulated with a few drops of hydrochloric acid, place it in a watch-glass, and let a second watch-glass be inverted over it, moistened with a drop of a solution of sulphuretted hydrosulphate of sulphide of ammonium (containing ammoniac disulphide); after a few minutes let the upper watch-glass be removed, and the liquid be evaporated to dryness by steam heat; potassic sulphocyanide will be left, and the volatile ammoniac sulphohydrate will pass off;  $(\text{H}_4\text{N})_2\text{S}_2 + \text{HCy} = \text{H}_4\text{NCyS} + \text{H}_4\text{NHS}$ ; let the dry residue be treated with a drop of a weak solution of ferric chloride; a red ferric sulphocyanide is formed under these circumstances.

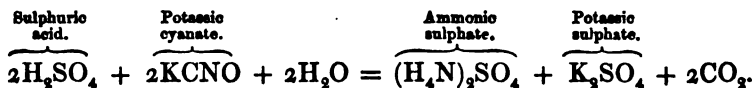
The cyanides of iron, cobalt, chromium, platinum, and some other metals, form, with the cyanides of the metals of the alkalis and the earths, compounds of a peculiar character, in which the presence of the iron, or the cobalt, &c., cannot be detected by the usual tests for these metals. Some of these compounds are of considerable importance, and will be noticed at a future point.

(504) CYANIC ACID; *Hydric cyanate*;  $\text{HCyO} = 43$ .—If cyanogen gas be passed into an alkaline solution, a change ensues something analogous to that which occurs when chlorine is similarly treated, cyanide and cyanate of the metal being produced; but the cyanic acid contains a smaller proportion of oxygen than chloric acid does;  $\text{Cy}_2 + 2\text{KHO} = \text{KCy} + \text{KCyO} + \text{H}_2\text{O}$ . If potassic carbonate be heated in cyanogen gas, a mixture of potassic cyanide and cyanate is formed, whilst carbonic anhydride is set free;  $\text{K}_2\text{CO}_3 + \text{Cy}_2 = \text{KCy} + \text{KCyO} + \text{CO}_2$ .

Potassic cyanate, however, is better prepared in a state of purity, by fusing potassic cyanide in a crucible, and adding litharge (plumbic oxide) in small quantities, till the oxide ceases to be decomposed;  $\text{KCy} + \text{PbO} = \text{KCyO} + \text{Pb}$ . The cyanate is easily separated from the reduced lead and the excess of plumbic oxide, which, from their superior density, sink through the melted mass to the bottom. The cyanate may be purified by solution in boiling alcohol, from which it crystallizes on cooling in deliquescent plates. Another but less productive method of preparing potassic cyanate consists in heating an intimate mixture of 2 parts of thoroughly dried potassic ferrocyanide with 1 part of finely powdered anhydrous black oxide of manganese: the mixture is

placed upon a sheet-iron plate and heated to dull redness, and the mass is kept constantly stirred. The oxidation of the cyanide is effected partly at the expense of the oxygen in the oxide of manganese, partly of that in the atmosphere. When the combustion has ceased, potassic cyanate may be dissolved out of the residue with hot alcohol.

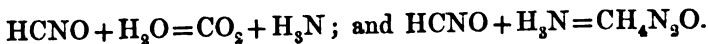
Potassic cyanate, if kept dry, may be preserved without change; but so unstable is the cyanic acid when uncombined with a fixed basyl, that on attempting to separate it from potassic cyanate by the addition of an excess of sulphuric or any other strong acid, traces of it only are obtained; a brisk effervescence ensues—each atom of the cyanic acid assimilates the elements of water, and is almost entirely resolved into 1 atom of ammonia, which remains in combination with the acid employed in decomposing the cyanate, and 1 atom of carbonic anhydride, which escapes with effervescence:—



Cyanic acid may be otherwise procured: viz., by distilling *cyanuric acid* ( $\text{H}_3\text{C}_3\text{N}_3\text{O}_3$ ), which is a crystallizable acid substance, 1 atom of which contains exactly the same elements as 3 atoms of cyanic acid. When this compound is sealed up in a bent glass tube, one limb of which is kept cool whilst heat is applied to the cyanuric acid in the other limb, a limpid, colourless liquid distils over and is condensed. The cyanuric acid is thus wholly converted into pure cyanic acid. Cyanic acid in its turn may be converted into the cyanuric, for if potassic cyanate be decomposed by the addition of two-thirds its equivalent of acetic acid, an acid cyanurate of potassium ( $\text{KH}_2\text{C}_3\text{N}_3\text{O}_3$ ) is formed.

Cyanic acid has an extremely pungent odour, and is very volatile; its vapour attacks the eyes powerfully, and when liquid it acts as a powerful caustic if incautiously dropped upon the skin. It is, however, impossible to preserve this compound, for in the course of a few hours it changes spontaneously, with evolution of heat, into a white enamel-like mass, which is permanent in the air, insoluble in water, and destitute of acid properties. To this body the name of *cyamelid* has been given; it has the same centesimal composition as the cyanuric and cyanic acids. Cyamelid may also be obtained by triturating potassic cyanate with crystallized oxalic or tartaric acid, and washing out the soluble salt of potassium. It may be converted by heat into cyanic acid; and if boiled with a solution of potash, gradually yields tripotassic

cyanurate; oil of vitriol decomposes it into carbonate of ammonium. A solution of cyanic acid in water quickly becomes decomposed into ammonic carbonate and urea ( $\text{CH}_4\text{N}_2\text{O}$ ):—



The cyanic is a monobasic acid. Solutions of the soluble cyanates give white precipitates with solutions of mercurous salts as well as with those of the salts of lead and of silver; they yield no precipitate with solution of corrosive sublimate, or with the solutions of salts of iron or of tin. With cupric nitrate they give a greenish-brown precipitate, and with auric chloride a brown precipitate.

(505) FULMINIC ACID.—Besides the remarkable oxides of cyanogen already mentioned, there is another acid which yields on analysis the same per-centage of its components as cyamelid, and the cyanic and cyanuric acids, though it possesses properties totally different from any of them. Its compounds explode with fearful violence. By dissolving 50 mgrms. of silver in 1 gramme of nitric acid diluted with about 2.5 grms. of alcohol, the new compound is deposited in crystals, which, when dry, detonate with the slightest friction; they consist of  $\text{Ag}_3\text{C}_2\text{N}_3\text{O}_3$ . The reaction by which this salt is produced is complicated; the nitrogen, however, is derived from the nitric acid, and the carbon from the alcohol.

Fulminic acid has not been obtained in an isolated form; on attempting to separate it from its salts by a more powerful acid, it is resolved into hydrocyanic acid and other bodies. Allusion will again be made to the fulminates when other compounds of cyanogen are described among the products of organic chemistry.


When the fulminates are boiled with a solution of sodic or potassic chloride, the acid is converted into another isomeric compound, termed *isocyanuric* or *fulminuric acid*. This body is but very slightly explosive.

(506) *Isomerism*.—The properties of these oxides of cyanogen serve to show clearly that mere identity in ultimate composition is not sufficient to produce identity of chemical character or properties; they place the doctrine of *isomerism* (or the existence of compounds identical in ultimate composition, but different in chemical properties) in a striking point of view. Numerous other instances will occur as we pursue further the study of the different compounds, not only of cyanogen, but of other bodies, and particularly of those which form the subject of organic chemistry.

There are various forms of isomerism; in some cases we have

no clue to the probable differences of molecular arrangement: in others there is every reason to suppose that the arrangement of the elementary molecules is on a totally different plan in the two bodies which are compared. Cyanic acid, for instance, may be represented as hydric cyanate ( $\text{H}_2\text{CNO}$ ); whilst it is certain that in cyamelid, which is insoluble, and presents nothing of the acid character, the arrangement of its constituents is quite different. Isomeric compounds, the equivalent numbers of which are identical, but of which the proximate constituents are different (like formic ether [ $\text{C}_2\text{H}_5\text{CHO}_2$ ] and methylacetic ether [ $\text{CH}_3\text{C}_2\text{H}_5\text{O}_2$ ]), are said to be *metameric*. In other cases, the differences in the properties of bodies which contain equal amounts of their constituents in 100 parts, may be simply explained upon the supposition that in the different compounds the state of condensation of these elements is different; bodies supposed to be thus constituted have been termed *polymeric*.

The following table contains a list of several different polymeric compounds of carbon and hydrogen which contain these two elements in the proportion of 1 atom of carbon to 2 atoms of hydrogen. Each of these bodies, however, possesses properties peculiar to itself: and if equal volumes of the vapour of each be compared, it will be found that the elements have undergone different degrees of condensation in the different compounds. As the density of the vapour increases, it has been observed that the boiling-point of such as are liquid rises proportionately. Supposing that one molecule of each compound gives off 2 volumes of vapour, the formulæ will be such as are contained in the subjoined table:—

Substances.	Formula. Mol. vol. = 	Density of vapour.		Boiling point.	
		Observed.	Calculated.	° C.	° F.
Olefiant gas (ethylene) ...	$\text{C}_2\text{H}_4$	0.978	0.967		
Propylene (tritylene) ...	$\text{C}_3\text{H}_6$	1.498	1.451		
Oil gas (tetrylene) ...	$\text{C}_4\text{H}_8$	1.852	1.934	- 18	0
Amylene ...	$\text{C}_5\text{H}_{10}$	2.386	2.418	39	102
Caproylene (hexylene) ...	$\text{C}_6\text{H}_{12}$	2.875	2.902	55	131
Heptylene ...	$\text{C}_7\text{H}_{14}$		3.385	50?	122 P
Octylene ...	$\text{C}_8\text{H}_{16}$	3.90	3.868	125	257
Eleene (nonylene) ...	$\text{C}_9\text{H}_{18}$	4.48	4.351		
Paramylene ...	$\text{C}_{10}\text{H}_{20}$	5.061	4.836	160	320
Cetylene ...	$\text{C}_{16}\text{H}_{32}$	8.007	7.736	275	527
Cerotylene ...	$\text{C}_{27}\text{H}_{54}$		12.159		
Melissylene ...	$\text{C}_{30}\text{H}_{60}$		14.508		

In this series, oil gas has double the density of ethylene, and

hence it must contain in the same volume of vapour twice as many elementary atoms. In like manner octylene contains twice as many atoms as oil gas, and four times as many as ethylene; cetylene, again, contains double the number of atoms of carbon and hydrogen in the same volume of vapour as octylene.

(507) PARACYANOGEN ( $C_2N_4P$ ).—The ordinary operation of preparing cyanogen gas from mercuric cyanide affords a good illustration of polymeric isomerism. After the mercury and the cyanogen have been expelled from the glass retort, there always remains a certain quantity of a brown matter, composed of nitrogen and carbon, combined in the same proportions as in cyanogen. *Paracyanogen*, as this brown body is called, is insoluble in water: it is neither volatile nor fusible, but like cyanogen it enters into combination with other elementary bodies, though the composition of the compounds so formed has been as yet but imperfectly studied.

In paracyanogen the carbon and nitrogen are more condensed than in cyanogen; so that if we regard cyanogen as composed of CN, paracyanogen, according to the experiments of Johnston, would consist of  $C_2N_4$ , its combining number being three times that of cyanogen, and the elements which compose it being more compactly united.

(508) CHLORIDES OF CYANOGEN.—Chlorine forms with cyanogen three polymeric compounds, all of which are highly poisonous: one is gaseous at the ordinary temperature of the air; the second is liquid, and the third is solid.

The *Gaseous Chloride of cyanogen*; *Cyanic chloride* ( $CyCl = 61.5$ ; *Rel. wt.* 30.75; *Theoretic Sp. Gr.* 2.126; *Mol. Vol.*  $\square$ ) is colourless: it has an intolerably pungent odour, and irritates the eyes powerfully; at  $0^\circ$  ( $-17.8^\circ C.$ ) it condenses in long prismatic needles, which fuse at  $5^\circ$  ( $-15^\circ C.$ ). Two volumes of the gas contain 1 volume of chlorine and 1 of cyanogen, united without condensation, so that its composition may be thus represented:—

			By weight.	By volume.	Sp. gr.
Cyanogen	...	...	Cy = 26 or 42.28	1 or 0.5 =	0.900
Chlorine	...	...	Cl = 35.5 57.72	1 0.5 =	1.226
Cyanic chloride	...	...	$CyCl = 61.5$ 100.00	2 1.0 =	2.126

Gaseous cyanic chloride is freely soluble in water, in ether, and in alcohol; the solution has no acid reaction, and does not precipitate argentic nitrate. It is obtained readily by transmitting a current of chlorine through a retort containing a mixture of powdered mercuric cyanide and water cooled to  $32^\circ$  ( $0^\circ C.$ ) by immersion in melting ice: the cyanic chloride is dissolved by the water; from this solution it may be expelled by the application of a gentle heat, and may be collected over mercury. According to Persoz, the gaseous cyanic chloride, if liquefied under the pressure of its own vapour, and preserved in tubes hermetically sealed, becomes gradually converted into a crystallized mass of the solid chloride.

*Liquid Chloride of cyanogen* [ $Cy_2Cl_2 = 123$ ; *Melting-pt.*  $19.4^\circ$  ( $-7^\circ C.$ ); *Boiling-pt.*  $60.8^\circ$  ( $16^\circ C.$ )] is procured by exposing diluted hydrocyanic acid cooled to  $32^\circ$ , to a gentle current of chlorine. After a while, a stratum of a liquid lighter than water is formed, and partially distils over into the receiver, which must be kept at  $32^\circ$ . This liquid must be washed with ice-cold water, and agitated in a freezing mixture with mercuric oxide to remove the excess of chlorine and hydrocyanic acid, after which it is rectified from calcic chloride (Wurtz). A very mobile colourless liquid, with an excessively irritating odour, resembling that of the gaseous chloride, is thus obtained; it is converted into a crys-

talline mass at  $19^{\circ} \cdot 4$  ( $-7^{\circ}$  C.). Liquid chloride of cyanogen is not soluble in water, but is freely soluble in alcohol.

*Solid Chloride of cyanogen* ( $\text{Cy}_2\text{Cl}_2 = 184^{\circ} \cdot 5$ ); *Sp. Gr. of Vapour*,  $6 \cdot 35$ ; *of Solid*,  $1 \cdot 32$ ; *Melting-pt.*  $284^{\circ}$  ( $140^{\circ}$  C.); *Boiling-pt.*  $374^{\circ}$  ( $190^{\circ}$  C.); *Mol. Vol.*  $\square$ ; *Rel. wt.*  $92 \cdot 25$ .—This substance crystallizes in white needles. It has a disagreeable odour like that of mice. The vapour of this compound is three times as dense as that of the gaseous chloride, it therefore contains 3 volumes of chlorine and 3 of cyanogen condensed into the space of 2 volumes. This chloride is but sparingly soluble in water, though it is freely taken up by alcohol and by ether. The solid cyanic chloride may be prepared by decomposing concentrated hydrocyanic acid by exposing it in a glass vessel with an excess of dry chlorine to the direct rays of the sun.

(508a) Bromine and iodine form solid crystalline compounds with cyanogen, corresponding in composition with the gaseous chloride; they may be obtained by distilling mercuric cyanide with bromine or with iodine.

Cyanogen combines directly with sulphuretted hydrogen in two proportions if the two gases are mixed in the presence of moisture; the first,  $2\text{CN}, \text{H}_2\text{S}$ , forms yellow crystals soluble in water, alcohol, and ether; the second,  $2\text{CN}, 2\text{H}_2\text{S}$ , is formed when cyanogen with an excess of sulphuretted hydrogen is transmitted into alcohol: it forms orange-red crystals sparingly soluble in cold water, but freely soluble in hot water, in alcohol, and in ether. When these compounds are boiled with dilute alkalis, water is taken up, and oxalic acid, ammonium, and sulphuretted hydrogen are formed; the second compound corresponding, in fact, to oxamide in which sulphur has taken the place of oxygen; for example,  $\text{C}_2\text{N}_2\text{H}_4\text{S}_2 + 4\text{H}_2\text{O} = (\text{H}_4\text{N})_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{S}$ . As will be seen hereafter, cyanogen is the nitrile of oxalic acid.

(509) There are other important compounds of cyanogen, the consideration of which will be more advantageously pursued at a future period; it will be sufficient at this point to indicate some of their leading chemical peculiarities.

Cyanogen, as we have seen, enters into combination with the non-metallic elements as though it were itself an elementary body. In this manner bodies such as the chlorides, the bromides, and the iodides of cyanogen may be obtained; they form well-defined compounds, which do not exhibit any special tendency to unite with other elements. In other cases, however, it is important to observe that many of the compounds to which cyanogen gives rise are themselves endowed with the property of uniting again, as though they were simple bodies, with other elements. With sulphur, for example, cyanogen forms a sulphide ( $\text{CNS}$ ), capable, in combination with the metals, of performing the part of a compound radicle, usually termed *sulphocyanogen* ( $\text{Scy}$ ), and of producing a series of salts, termed sulphocyanides, many of which may be crystallized: of this potassic sulphocyanide,  $\text{KCNS}$  or  $\text{K}, \text{Scy}$ , furnishes an instance. Similar compound radicles are furnished also by the union of cyanogen with many of the metals themselves; in this way iron in the *ferrocyanides* and cobalt and chromium in the *cobaltcyanides* and *chromicyanides* forms a



compound group, or salt radicle, which, when it unites in its turn with other metals, performs the functions of a simple body, such as chlorine or iodine: an example of this is seen in the well-known yellow prussiate of potash, or potassic ferrocyanide, ( $K_4FeCy_6$ ), in which the compound of iron and cyanogen,  $FeCy_6$ , may be viewed as a compound radicle known as *ferrocyanogen* ( $Fcy$ ).

#### § V. GENERAL REMARKS ON THE DISCRIMINATION OF THE GASES FROM EACH OTHER.

(510) Having now described all the gaseous compounds which are of any considerable importance, with the exception of two—viz., arseniuretted hydrogen and antimoniuiretted hydrogen,—it will be advantageous to take a brief review of their general characters before passing to the consideration of the metals and their compounds.\*

There are about 30 bodies which are permanently gaseous at the mean temperature of the atmosphere. Several of these compounds are met with in the uncombined form in the atmosphere, either uniformly, or under particular circumstances not of unfrequent occurrence; these gases are oxygen, nitrogen, carbonic and sulphurous anhydrides, hydrosulphuric acid, ammonia, and occasionally carbonic oxide and light carburetted hydrogen. Generally speaking, the different gases, when pure, are readily distinguished from each other by some well-marked physical or chemical property. The few gases which are coloured are at once indicated by the peculiarity of their tint, conjoined with their characteristic odour: in this manner peroxide of nitrogen, chlorine, hypochlorous and chlorous anhydride, peroxide of chlorine, and vapour of bromine are at once recognized.

Many gases have a peculiar and characteristic odour. Some of the most important, however, including oxygen, nitrogen, hydrogen, carbonic anhydride, carbonic oxide, light carburetted hydrogen, olefiant gas, and nitrous oxide possess little or no odour, and require other means for discriminating them from each other.

(511) In order to aid the operator in distinguishing the different gases from each other, Thénard divided them into four groups, the arrangement being dependent upon the action of a

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\* Methyl, ethyl, and trityl, with their hydrides, as well as tritylene and acetylene, are occasionally present in coal-gas, but they will not here be specially noticed, because these hydrocarbons cannot be distinguished from each other except by analysis. Acetylene may be absorbed by passing the gas which contains it through an ammoniacal solution of cupreous chloride, when a flocculent red deposit of acetylide of copper is gradually formed.

solution of potash upon them, conjoined with the occurrence or the absence of combustion on the application of a lighted match to the gas. The action of potash is ascertained by admitting a few drops of a solution of potash into a test-tube filled with the gas, and standing over mercury : on agitating the contents of the tube, it is immediately obvious whether any absorption occurs. The application of a lighted match to another small tube filled with the gas shows whether it be inflammable, or whether it extinguishes or supports combustion.

The four groups of gases which are formed by the application of these tests are the following:—

1. Gases which are absorbable by potash, but which are not inflammable.
2. Gases absorbable by potash, but which are inflammable.
3. Gases not absorbable by potash, and not inflammable.
4. Gases not absorbable by potash, which are inflammable.

We proceed to point out briefly the characters of the components of each group.

(512) 1.—*Gases which are absorbable by Potash, but are not inflammable*; these are 15 in number:—viz.,

- |                           |                            |
|---------------------------|----------------------------|
| 1. Hydrochloric acid      | 9. Nitrous anhydride       |
| 2. Hydrobromic acid       | 10. Peroxide of chlorine   |
| 3. Hydriodic acid         | 11. Chlorous anhydride     |
| 4. Silicic fluoride       | 12. Hypochlorous anhydride |
| 5. Boric fluoride         | 13. Chlorine               |
| 6. Boric chloride         | 14. Carbonic anhydride     |
| 7. Carbonic oxydichloride | 15. Cyanic chloride.       |
| 8. Sulphurous anhydride   |                            |

Of these gases each of the first eleven reddens litmus-paper, when moistened and plunged into it. Hypochlorous anhydride and chlorine destroy its colour, and bleach it entirely. Carbonic anhydride is nearly without action, and cyanic chloride produces no effect upon its colour. The first six gases fume strongly when mixed with the air, owing to their action on the moisture which it contains: the solutions in water of hydrochloric, hydrobromic, and hydriodic acids are immediately distinguished by the usual tests for them. Each gas also presents certain peculiarities—viz., 1.—A small quantity of chlorine produces no change in the hydrochloric gas; 2.—In hydrobromic gas it occasions the separation of red fumes of bromine; and 3.—In the hydriodic gas violet fumes of iodine appear. 4.—Silicic fluoride is recognized by the gelatinous deposit of silica which water produces

when the gas is dissolved in this liquid. 5.—Boric fluoride produces a gelatinous precipitate in a solution of potash, but not in pure water. 6.—Boric chloride is decomposed by water into hydrochloric and boracic acids, which may be recognized in the solution by the appropriate tests. 7.—Carbonic oxydichloride has a peculiar, pungent odour, and is decomposed by water into hydrochloric acid and carbonic anhydride. 8.—Sulphurous anhydride is immediately recognized by the suffocating odour of a burning sulphur match: it is absorbed by the peroxide of lead, and a white plumbic sulphate is formed. 9.—Nitrous anhydride is sufficiently characterized by its colour and peculiar odour; and 10, the same may be remarked of peroxide of chlorine. 11.—Chlorous anhydride has a greener tinge than the peroxide of chlorine, and it yields a bright yellow solution when dissolved in water. 12.—Hypochlorous anhydride has the odour of the bleaching compounds of chlorine with the alkalies and earths, and it rapidly destroys vegetable colours: these three oxides of chlorine detonate by the application of a temperature below that of boiling water. 13.—Chlorine is distinguished by its green colour and remarkable odour, by its bleaching action on vegetable colours, and by its sparing solubility in water, which takes up about twice its bulk of the gas. 14.—Carbonic anhydride extinguishes flame, renders lime-water turbid, and is soluble in about its own bulk of water. 15.—Cyanic chloride is recognized by its pungent odour, and its peculiar irritating effect on the eyes.

(513) 2.—*Gases absorbable by Potash and inflammable*; these are only 4 in number:—viz.,

- |                           |  |                         |
|---------------------------|--|-------------------------|
| 1. Sulphuretted hydrogen  |  | 3. Telluretted hydrogen |
| 2. Seleniuretted hydrogen |  | 4. Cyanogen.            |

These gases are recognized with great facility. 1.—Sulphuretted hydrogen has a peculiar odour of putrid eggs; it burns with a blue flame, often attended with a deposit of sulphur: it blackens paper soaked in a solution of plumbic acetate, and is decomposed by moist chlorine, with separation of sulphur; water dissolves about twice its bulk of the gas. 2.—Seleniuretted hydrogen has an odour analogous to that of the preceding gas; its aqueous solution gradually deposits selenium in the form of a red amorphous precipitate: it precipitates salts of zinc of a flesh-red colour. 3.—Telluretted hydrogen is also decomposed by chlorine, tellurium being set free, and subsiding as a brown powder. 4.—Cyanogen burns with a rose-edged purple flame; it has a penetrating characteristic odour. If mixed with an equal

volume of oxygen, and a red-hot platinum wire be suspended in the mixture, red nitrous fumes are produced by the oxidation of the nitrogen contained in the gas.

(514) 3.—*Gases not absorbable by Potash, and not inflammable*; of these also there are four—viz.,

- |                  |  |                  |
|------------------|--|------------------|
| 1. Oxygen        |  | 3. Nitrogen      |
| 2. Nitrous oxide |  | 4. Nitric oxide. |

1.—Oxygen is at once distinguished from all other gases by its property of kindling a glowing match, by its power of producing red fumes when mixed with nitric oxide, and by its insolubility in water when agitated with it. It is absorbed by moistened phosphorus; by a solution of cupreous oxide in ammonia, rendering the colourless solution deep blue; and by a solution of pyrogallic acid in potash, the mixture becoming of an intense bistre colour. Solutions of the sulphides of the alkali-metals also absorb oxygen rapidly. 2. Nitrous oxide, though it rekindles a glowing match, is dissolved when agitated with water. 3.—Nitrogen extinguishes the flame of burning bodies; it is insoluble in water, and does not render lime-water turbid. 4.—Nitric oxide is instantly recognized by the red fumes which it occasions when mixed with air or free oxygen; it is immediately absorbed by a solution of ferrous sulphate, giving the liquid a deep brown colour when oxygen is present.

(515) 4.—*Gases not absorbable by Potash, which are inflammable*; these gases are 7 in number:—viz.,

- |                               |  |                           |
|-------------------------------|--|---------------------------|
| 1. Hydrogen                   |  | 5. Phosphuretted hydrogen |
| 2. Light carburetted hydrogen |  | 6. Arseniuretted hydrogen |
| 3. Olefiant gas               |  | 7. Carbonic oxide.        |
| 4. Oil-gas                    |  |                           |

1.—Hydrogen is inodorous, if pure; it burns with a feebly luminous flame, and if mixed with half its volume of oxygen, produces water either by the transmission of an electric spark, or by the action of a ball of spongy platinum. 2.—Light carburetted hydrogen burns with a yellowish flame; it is not acted upon if mixed with chlorine over water and screened from light, and is not dissolved by fuming sulphuric acid. 3.—Olefiant gas, when mixed with an equal volume of chlorine, even in the dark becomes condensed to an oily liquid which is insoluble in water; it is also absorbed by antimoniac pentachloride and by the Nordhausen sulphuric acid: it burns with a brilliant smoky flame. 4.—Oil-gas is soluble in oil of vitriol, and in alcohol; it burns with a brilliant smoky flame. When the last two gases are mixed together,

there is considerable difficulty in identifying the existence of each in such a mixture, and a still greater difficulty occurs when either acetylene or methyl, ethyl, trityl, or their hydrides, are present. 5.—Phosphuretted hydrogen is distinguished by its peculiar alliaceous odour: it burns with a luminous flame, producing white fumes of phosphoric anhydride; solutions of the salts of copper, silver, and mercury dissolve it and form brown precipitates. 6.—Arseniuretted hydrogen is decomposed if passed through glass tubes heated nearly to redness, a ring of arsenicum being deposited: it burns with a peculiar white flame, and deposits a brown stain of arsenicum on cold bodies introduced into the burning jet. It is extremely poisonous, and has a peculiar odour of garlic. It may be distinguished from antimoniuiretted hydrogen by methods to be described hereafter (846). 7.—Carbonic oxide burns with a pale blue flame, producing carbonic anhydride; it is insoluble in water, and is dissolved by a solution of cupreous chloride in hydrochloric acid.

(516) *General Principles of the Analysis of a Mixture of Gases.*

—In a mixture of gases a qualitative examination must be made as a preliminary step, in order to ascertain what gases are present. It is of course needless to search for those which condense or decompose each other. Ammonia, for example, would not be found in a mixture which contained hydrochloric, hydriodic, or hydrobromic acid gases, nor in the presence of sulphurous or nitrous anhydrides. Oxygen would not occur in a mixture in which nitric oxide was present. Neither could free chlorine or its oxides co-exist with hydriodic or hydrobromic acid, nor with olefiant gas, nor with the compounds of hydrogen with sulphur, selenium, tellurium, phosphorus, or arsenic: chlorine and its oxides are equally incompatible with ammonia.

The complete analysis of a mixture of different gases is one of the most delicate and difficult branches of chemical analysis, and it is not intended on the present occasion to attempt to give more than an idea of the principles on which such an operation is conducted, and of the apparatus by which it is effected.

As an illustration of the method of proceeding we may take a case of frequent occurrence: viz., the determination of the composition of a sample of coal-gas. In this gas, the ingredients which may be present are numerous. These are—1, hydrogen; 2, olefiant gas and other heavy hydrocarbons; 3, light carburetted hydrogen; 4, carbonic oxide; 5, carbonic anhydride; 6, sulphuretted hydrogen; 7, ammonia; 8, oxygen; and 9, nitrogen, the last two derived from the atmosphere.

A qualitative examination is made thus:—the proportion of ammonia and of sulphuretted hydrogen is usually very minute, and in most cases these gases must be sought for by placing the tests for their presence for some time in a current

of the coal-gas. In searching for ammonia, a piece of moistened litmus-paper, feebly reddened, is placed for a minute in a jet of the issuing gas: if the blue colour be restored, ammonia is present. Paper soaked in a solution of plumbic acetate may be subjected to a similar trial: if it turn brown, sulphuretted hydrogen is present. The presence of oxygen is detected by admitting a bubble of the nitric oxide into a tube filled with the gas under trial, and looking through the tube obliquely upon a sheet of white paper; very small traces of oxygen may thus be detected by the red tinge produced, owing to the formation of peroxide of nitrogen. Carbonic anhydride may be detected by the turbidity which it produces in lime-water or in a solution of basic plumbic acetate, if thrown up into the gas, whilst standing in a tube over mercury. The existence of the other gases may be assumed, for they are certain to be present, in greater or less quantity. The sulphuretted hydrogen and ammonia are too small in amount to be quantitatively determined; but supposing that oxygen and carbonic anhydride are found to be present, the proportion of seven different gases will remain to be ascertained. The following method may be adopted for their quantitative determination:—

1. *Carbonic Anhydride*.—A volume of the gas is confined over mercury, and its bulk is measured, with due attention to temperature and pressure. A piece of caustic potash which has been melted upon the end of a long platinum wire, to serve as a handle, is introduced from below, through the mercury into the tube. Care must be taken that the wire does not project above the surface of the mercury in the trough, otherwise a slow process of diffusion will occur between the gas in the tube and the outer air. After two or three hours the potash is withdrawn; the amount of the absorption indicates the proportion of carbonic anhydride which was present.

2. *Olefiant Gas and Heavy Hydrocarbons*.—These gases are absorbed by introducing another ball, consisting of porous coke moistened with fuming sulphuric acid. It is necessary, however, before reading off the volume of the gas, to introduce a ball of potash a second time, in order to withdraw the vapour of sulphuric anhydride, which possesses sufficient volatility to introduce a serious error by dilating the bulk of the gas unless it be completely removed. The total amount of absorption will indicate the proportion of olefiant gas, together with the vapours of condensable hydrocarbons.

3. *Oxygen*.—This gas is determined in a similar manner, by employing a ball of moist phosphorus, which must be left in the gas for twenty-four hours; the fresh diminution in bulk, shows the proportion of oxygen.\*

4. *Carbonic Oxide*.—The accurate separation of carbonic oxide from the other gases is not easily effected. The gas may be divided into two portions, one of which is to be carefully measured as it stands over mercury, in the jar, *λ*, fig. 295, p. 64: a small quantity of a solution of cupreous chloride in hydrochloric acid is next added by means of the syringe, *i*, and the mixture is briskly agitated; the gas is then withdrawn by means of the gas pipette, also shown in fig. 295, and transferred by its means to a second graduated tube, also standing over mercury; into this tube a ball of caustic potash on the end of a platinum

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\* A ball of coke moistened with a concentrated solution of potash and pyrogalllic acid may be employed for the same purpose: the absorption in this case is much more rapid.

The use of pellets of appropriate materials may be extended to other gases: for example—*Sulphurous anhydride* may be absorbed by using a ball of moistened peroxide of manganese, or of peroxide of lead; and *hydrochloric acid* is rapidly absorbed by a ball consisting of crystallized rhombic hydrosulphic phosphate.

wire is introduced, for the purpose of absorbing the vapours of hydrochloric acid with which the gas is saturated; its bulk may then be read off, and the volume of carbonic oxide may be known by the loss in bulk which it has experienced.

The absorption of gases by liquid reagents is much more rapid than when moistened balls are employed, and provided that only very small volumes of liquid are used, the results are equally accurate. Carbonic anhydride may be thus absorbed by means of a concentrated solution of caustic potash, one or two drops of which will suffice; and oxygen may be withdrawn by a concentrated mixture of pyrogallic acid and caustic potash.

5, 6, 7. *Nitrogen, Carburetted Hydrogen, and Hydrogen*.—The determination of the carbonic oxide, however, may be effected along with the carburetted hydrogen and hydrogen without having recourse to absorption. Let a portion of the gas in which the carbonic oxide is still present be now transferred to a siphon endiometer (fig. 290, p. 54), and let its bulk,  $V$ , be accurately measured; then add about twice its volume of oxygen, and measure the gas a second time; let this bulk be  $V_1$ ;  $V_1 - V$  will give the volume of oxygen which has been added. Let  $V_2$  be the bulk of the gas after the mixture has been exploded by the transmission of the electric spark:  $V_1 - V_2$  indicates the diminution in bulk which it has experienced: call this  $a$ . Then inject a small quantity of a strong solution of potash, and again note the volume,  $V_3$ . The absorption,  $V_2 - V_3$ , will be due to the quantity of carbonic anhydride which has been formed: call this  $b$ . The remaining gas,  $V_3$ , consists of oxygen in excess and nitrogen. The quantity of oxygen in excess is ascertained by mixing the residual gas with about twice its bulk of hydrogen, and causing the electric spark to pass a second time. Let the volume of the mixture before firing be  $V_4$ , and let  $V_5$  be the bulk after firing:  $V_4 - V_5$  will represent the amount of condensation; and one-third of this, or  $\frac{V_4 - V_5}{3}$  will be due to the excess of oxygen. On deducting this from the residue,  $V_3$ , the difference gives the volume of nitrogen,  $n$ ;  $V_3 - \frac{V_4 - V_5}{3} = n$ . The difference between the amount of the oxygen thus found to be in excess, and that originally introduced, will of course represent the quantity of oxygen consumed: call this  $c$ : thus  $V_1 - V - \frac{V_4 - V_5}{3} = c$ .

Assuming that the temperature of the gas has not varied in the course of the experiment, which may be ensured by due precautions, we have now all the data for calculating the proportions of carburetted hydrogen, of hydrogen, and of carbonic oxide, which are present in the mixture.

Let  $x$  represent the quantity of light carburetted hydrogen; this gas requires twice its own volume of oxygen for complete combustion, and furnishes its own volume of carbonic anhydride, which requires for its formation an equal volume of oxygen, or half the amount consumed; whilst the other half of the oxygen is required by the hydrogen which is condensed in the form of water;  $2x$  will consequently represent the diminution in bulk of oxygen which occurs on detonation, due to the amount of carburetted hydrogen which is present.

Again, when hydrogen is converted into water, it requires half its bulk of oxygen, and both are condensed entirely. If  $y$  represent the bulk of the hydrogen,  $\frac{3y}{2}$  will be the diminution in bulk of the mixed gases on detonation, which is occasioned by the hydrogen in the mixture.

Let  $z$  represent the volume of carbonic oxide present; carbonic oxide for its conversion into carbonic anhydride requires half its bulk of oxygen, the carbonic anhydride produced occupying the same bulk as the carbonic oxide.  $\frac{a}{2}$  will therefore indicate the condensation which occurs on firing the mixture, owing to the carbonic oxide present.

The total condensation in bulk,  $a$ , which occurs on firing a mixture of light

carburetted hydrogen, hydrogen, and carbonic oxide, will consequently admit of being thus represented :—

$$(1) \quad a = 2x + \frac{3y}{2} + \frac{z}{2}.$$

Further, the quantity of the carbonic anhydride,  $b$ , formed by the detonation, is composed of a volume of carbonic anhydride equal in bulk to the light carburetted hydrogen, and a volume equal to that of the carbonic oxide, so that the total quantity of carbonic anhydride may be thus indicated :—

$$(2) \quad b = x + z.$$

And lastly, the oxygen consumed,  $c$ , will be composed of the following quantities : by light carburetted hydrogen, twice its bulk,  $2x$ ; by hydrogen, half its bulk,  $\frac{y}{2}$ ; and by carbonic oxide half its bulk,  $\frac{z}{2}$ ; or the total quantity of oxygen consumed will be the following :—

$$(3) \quad c = 2x + \frac{y}{2} + \frac{z}{2}.$$

From these three equations the values of  $x$ ,  $y$ ,  $z$  are determined :—

$$x = c - \frac{a+b}{3};$$

$$y = a - c;$$

$$z = \frac{a+4b}{3} - c.$$

Minute directions for the analysis of various gaseous mixtures are given by Regnault in the fourth volume of his *Cours Élémentaire de Chimie*, which contains a description of a form of eudiometer well adapted for accurate experiments; this eudiometer has been advantageously modified by Frankland and Ward (*Q. J. Chem. Soc.* vi. 197). Bunsen has also introduced very important improvements into the manipulation and apparatus required for the analysis of gases, which are fully detailed in his *Gasometry*, translated by Roscoe (*see* also the article on Eudiometry, in Liebig and Poggendorff's *Handwörterbuch der Chemie*, vol. ii.); and the modes of manipulation have been still further simplified by Williamson and Russell.

## CHAPTER XI.

### B. SECOND DIVISION.—THE METALS.

#### § I.—GENERAL PROPERTIES OF THE METALS.

(517) *General Characters of the Metals.*—The metals, as a class, are characterized by a peculiar lustre termed the *metallic* lustre. They are possessed of a high degree of opacity, and are good conductors both of heat and electricity. Some of them are also endowed with the properties of ductility, or fitness for drawing into wire, and of malleability, or extensibility under the hammer. Many of them have a high specific gravity. When separated from



their compounds by electrolytic action, they appear at the platinum, or negative wire of the voltaic battery.

These properties are not developed equally in all the metals; in some metals one or more of them may be wanting altogether: and there are other substances, not metallic in their nature, in which some of these characters are strongly displayed.

(518) *Lustre, Opacity, and Colour*.—Although, when polished, all metals present the lustre termed metallic, yet most of them may be obtained by minute subdivision in a form devoid of lustre. Iron, copper, platinum, gold, silver, and even mercury, may be readily procured in this condition by processes to be mentioned hereafter.

If, however, these metallic powders be subjected to pressure under the burnisher, a sufficient approximation of their particles is produced to render them capable of reflecting light, and the metallic lustre reappears. This property admits of being applied in the fine arts; for instance, it is possible to make copies of medals or ancient coins, by employing finely-divided copper, which is introduced with the medal into a mould: by submitting it to pressure, an exact copy of the medal, with a beautifully polished surface, is obtained: the copy is then strongly heated, care being taken to exclude atmospheric air: during the ignition the copy shrinks a little in all directions, but a fac-simile is formed, which is extremely distinct, though reversed, and a little smaller than the original.

Bodies which are not metallic occasionally assume a brilliant surface like the metals. Iodine, which in all its chemical relations is directly opposed to the metals, yet possesses a strong lustre; the same thing is observable in a form of carbon, termed by the workman *kish*, which escapes from the vent-holes of the moulds during the process of casting iron. The native form of carbon, known as graphite or plumbago, has received its popular name of *black-lead* from its metallic appearance.

Metals are among the most opaque bodies with which we are acquainted: but their opacity is not perfect. When reduced to exceedingly fine leaves, a portion of light is transmitted; for example, pure gold, of not more than  $\frac{1}{800,000}$  inch, or 0.<sup>mm</sup>.0000125 thick, allows a green light to pass.

The *colour* of the reflected light varies with the nature of the metal. In most cases it is nearly white, with a shade peculiar to each metal: the tints of silver, platinum, tin, cadmium, and palladium, are nearly alike; other metals, such as lead and zinc, have a bluish colour; others, like iron and arsenicum, have a greyish

hue ; calcium and barium are pale yellow ; gold is a full yellow ; and copper is of a red colour. By repeated reflections from the same metal a distinct colour is often rendered obvious, though it is not seen upon looking at the polished surface. A red tint may thus be made evident in silver, and a violet tinge in steel.

Some of the metals possess a characteristic *odour* ; iron, tin, and copper emit, on friction, a smell peculiar to themselves, and arsenicum, when volatilized, evolves a powerful odour of garlic. The taste of most of the soluble compounds of the metals is astringent or acrid, and of the peculiar kind termed metallic.

(519) *Hardness, Brittleness, and Tenacity*.—Great differences are observable between the *hardness* of the different metals ; steel may be rendered hard enough to scratch glass, while lead will take impressions from the finger-nail, and potassium may be spread like butter. Many of the harder metals are very elastic and sonorous when struck ; but these properties are more strikingly displayed in some of the alloys, or compounds of the metals with each other, as in the alloy of tin and copper used for bells, and in the combination of carbon with iron, well known as steel, which, by its high elasticity, is pre-eminently qualified for the construction of the springs used in machinery.

Closely connected with the hardness are the *brittleness* and the *tenacity* of metals, which are very variable. Some, like antimony, arsenicum, and bismuth, may be pulverized without difficulty in a mortar, while others, as iron, gold, silver, and copper, require great force to effect their disintegration. The brittleness of some of the metals is materially affected by temperature. Zinc, within the ordinary atmospheric range, is so brittle that it cannot be bent at a sharp angle without danger of destroying its cohesion, while if heated to between  $200^{\circ}$  and  $300^{\circ}$  (or from about  $95^{\circ}$  to  $150^{\circ}$  C.) it may be wrought with facility. Brass, an alloy of copper and zinc, on the contrary, becomes brittle at temperatures approaching to redness, but while cold it possesses considerable malleability.

Taking the tenacity of lead = 1, the tenacity of the different metals, after annealing, will be represented according to Wertheim's experiments as follows :—

Lead . . . . .	1	Silver . . . . .	8.9
Cadmium . . . . .	1.2	Platinum . . . . .	13
Tin . . . . .	1.3	Palladium . . . . .	15
Gold . . . . .	5.6	Copper . . . . .	17
Zinc . . . . .	8	Iron . . . . .	26

The tenacity of the metals has been measured by fixing firmly in a vice one

end of a bar or wire of the metal, the strength of which is to be ascertained, and attaching to the other end a convenient support for weights which are cautiously increased until the wire breaks. By comparing together the weights required to determine the rupture of the different metals for bars of equal section, a comparative table of tenacity may be formed. Various circumstances materially influence the strength of the same metal;\* such as its purity, the mode in which the bar has been prepared (whether by casting, by forging, or by wire-drawing), the temperature at which the comparisons are made, the application or omission of the process of annealing, and the manner in which the tension has been exerted, whether gradually or suddenly. Different observers, in consequence of operating differently in some one or other of these respects, have obtained results which vary from each other considerably. The necessity of attention to these points will be evident on examining the results obtained by Wertheim (*Ann. de Chimie*, III. xii. 440), who has given an elaborate series of experiments upon the tenacity of different metals, the most important of which are embodied in the following table. The numbers represent the weight in kilogrammes which a bar of each metal of 1 square millimetre in section would support without breaking, both when the strain is gradually increased and when suddenly applied:—

Metal employed.	59° F. (15° C.)		212° F. (100° C.)	392° F. (200° C.)
	Gradual.	Sudden.		
Cast steel, drawn ...		83·8		
" annealed ...	65·7			
Piano wire (steel) ...	70·0	99·1		
" annealed ...	40·0	53·9	59·10	50·90
Iron wire ...	61·10	65·1		
" annealed ...	46·88	50·25	51·10	46·9
Copper wire ...	40·30	41·0		
" annealed ...	30·54	31·68	22·10	
Platinum wire ...	34·10	35·0		
" annealed ...	23·50	27·70	22·60	19·70
Palladium wire ...		27·2		
" annealed ...	27·4			
Silver wire ...	29·0	29·6		
" annealed ...	16·02	16·5	14·00	14·00
Zinc, commercial, drawn ...	12·80	15·77		
" " annealed ...		14·40	12·20	7·27
Pure zinc, cast ...	4·5			
Gold drawn ...	27·0	28·4		
" annealed ...	10·08	11·1	12·60	12·06
Cadmium, drawn ...	2·24			
" annealed ...		4·81	2·60	
Lead, cast ...	1·25	2·21		
" drawn ...	2·07	2·36		
" annealed ...	1·80	2·04	0·54	
Tin, drawn ...	2·45	3·0		
" " annealed ...	1·70	3·62	0·85	

\* Deville, for example, by melting cobalt in a crucible of lime, has obtained it free from carbon and other impurities, in the form of a ductile mass of such tenacity as to furnish a wire capable of supporting twice as great a weight as a wire of pure iron of similar dimensions; and a wire of nickel prepared in a similar way, though inferior in tenacity to one of cobalt, surpassed one of iron in the ratio of 3 to 2.

It will be seen, from an inspection of this table, that the general effect of heat is to diminish the tenacity of the metals, except in the case of iron, steel, and gold, the tenacity of which seems to be somewhat increased by heating them to the temperature of boiling water; this is particularly so with iron: by a further elevation of temperature the tenacity is again diminished. The influence of annealing, or heating the bar to dull redness and allowing it to cool slowly, is still more remarkable, for by this means the tenacity of gold is reduced more than half, that of silver nearly as much, that of platinum about one-third, and that of iron and copper about a fourth.

According to Wertheim all circumstances which increase the density, as a rule increase the elasticity also. He finds the coefficient of elasticity of an alloy to be sensibly the mean of the coefficients of the metals which enter into its composition, even when the formation of the alloy is attended with change of volume. The transmission of a current of electricity produces a momentary diminution in the elasticity, independently of the diminution caused by the rise of temperature which it occasions.

(520) *Malleability and Ductility*.—The following metals are termed malleable metals, i.e. metals which may be reduced to thin leaves either by lamination between rollers, or by hammering:—

1. Gold	6. Iron	10. Lead
2. Silver	7. Aluminum	11. Cadmium
3. Copper	8. Tin	12. Nickel
4. Platinum	9. Zinc	13. Cobalt.
5. Palladium		

Lithium, potassium, and sodium, as well as mercury when in a frozen state, and thallium, likewise admit of extension under the hammer. Gold far surpasses all the other metals in malleability, being capable of reduction into leaves so thin that a square decimetre weighs less than 20 mgrms., or a square foot weighs less than 3 grains, and the film does not exceed the 280,000th of an inch in thickness. Silver and copper may also be reduced to leaves of great tenuity. The other metals may be rolled into foil, but cannot be hammered into leaf. At the Industrial Exhibition of Breslau, 1852, an album of leaf iron was exhibited, the sheets of which did not exceed 0.01<sup>mm</sup> in thickness, and a square decimetre of the leaf weighed only 776 mgrms. Quite recently Messrs. Hallam and Co. are said to

have obtained leaves of iron of less than half this thickness; the sheets did not exceed  $\frac{1}{800}$  inch in thickness, or  $\frac{1}{180,000}$  mm., and a square inch weighed only 0.36 grain. Nickel and cobalt are far less malleable than the other metals in the list. The metals become denser in rolling, and are often rendered so hard by the operation that they require to be annealed between every second or third rolling. During the processes of hammering and rolling, much heat is extricated.

The metals may be arranged in the following order of ductility, the property being possessed to a nearly equal extent by the first five upon the list:—

1. Gold	7. Cadmium	12. Tin
2. Silver	8. Cobalt	13. Lead
3. Platinum	9. Nickel	14. Thallium
4. Iron	10. Aluminum	15. Magnesium
5. Copper	11. Zinc	16. Lithium.
6. Palladium		

Ductility is peculiarly displayed by the first 7 metals on the list. Wollaston procured a wire of platinum, the diameter of which did not exceed the  $\frac{1}{30,000}$  of an inch, or 0.00083 millim., by placing a wire of platinum in the axis of a small cylinder of silver and reducing the compound wire to the utmost practicable tenuity in the ordinary way, by drawing it through holes made in a hard steel plate, termed a draw-plate; the apertures through which the wire was made to pass diminishing in size by regular gradation. Both metals were thus attenuated, *pari passu*, and the silver was finally dissolved off by nitric acid, which left the platinum unacted upon. Gold wire equally fine was obtained by a similar process (*Phil. Trans.* 1813). Steel wires of extreme fineness have been produced in a similar manner, the coating of silver, in this case, having been dissolved by the action of mercury. Zinc, tin, lead, magnesium, and even lithium, may also be obtained in the form of wire, but with difficulty, on account of their feeble tenacity. Matthiessen has succeeded in obtaining many of the softer metals such as sodium and lithium, in the form of wire, by forcing them under strong pressure through an aperture in a steel die.

The malleability of a metal is by no means always proportioned to its ductility; iron, though it may be reduced to wires of extreme fineness, is not nearly so malleable as gold, silver, copper, and some other metals which are inferior to it in ductility. A few substances which are not metallic exhibit, when in

a state of semifusion, a very perfect ductility. Half-melted glass shows this property in a marked degree; it may be spun into very fine threads, which have even been woven into a species of cloth, designed for ornamental purposes.

It is obvious that the properties of brittleness, tenacity, ductility, and malleability, must be materially dependent upon the texture of the metal. This is strikingly exemplified in the variation in tenacity exhibited by the same metal under different circumstances. Silver, in ordinary cases, is tough, ductile, and malleable; by repeated heatings and coolings, however, its particles arrange themselves in a crystalline manner, and it then becomes very brittle. Copper, when deposited in crystals by slow voltaic action, is very hard and brittle; but when the action is more rapid it is soft and tough, and the metal then exhibits a fibrous character. It may indeed be stated, as a general principle, that the crystalline metals, such as zinc, antimony, bismuth, and arsenicum, are the most brittle; while those which, like iron, have a fibrous structure, are possessed of a high degree of tenacity.

The structure of a metal is easily displayed in many cases, by placing it in solvents the operation of which is very gradual. Some of the metals which fuse readily may be obtained in crystals without difficulty, by allowing 2 or 3 kilos. of the melted metal to cool slowly, and pouring out the interior portions before the whole has had time to solidify; the walls of the cavity are then found to be lined with crystals on their inner surface. Bismuth is particularly well adapted to this process. The less fusible metals, such as copper, iron, and silver, may often be crystallized from their solutions by slow voltaic actions. Many of them—as, for example, gold, silver, and copper—occur native in crystals. A large proportion of the metals crystallize in forms belonging to the regular system.

(521) *Specific Gravity*.—Wide differences are observable in the specific gravity of the metals. In the annexed table, variations are exhibited between the extremes of iridium and platinum, the heaviest known forms of matter, on the one hand, and lithium on the other, which has little more than half the density of water. The lighter metals are all characterized by their powerful attraction for oxygen; those which are least oxidizable possessing generally the highest specific gravity. In a few instances, the most marked of which is platinum, the density may be somewhat increased by rolling and hammering; but this is not usually the case.

*Specific Gravity of the Metals.*

Metal.	Sp. gr.	Observer.
Platinum ... ..	21.53	Wollaston.
Osmium ... ..	21.4	Deville and Debray.
Iridium ... ..	21.15	Deville and Debray.
Gold ... ..	19.34	G. Rose.
Uranium ... ..	18.4	Péligot.
Tungsten ... ..	17.6	D'Elhuyart.
Mercury ... ..	13.596	Regnault.
Rhodium ... ..	12.1	Deville and Debray.
Thallium ... ..	11.91 to 11.81	Crookes.
Palladium ... ..	11.8	Wollaston.
Ruthenium ... ..	11.4	Deville and Debray.
Lead ... ..	11.36	Reich.
Silver ... ..	10.53	G. Rose.
Bismuth ... ..	9.799	Marchand and Scheerer.
Cobalt ... ..	8.95	Rammelsberg.
Copper ... ..	8.95 to 8.92	Marchand and Scheerer.
Nickel ... ..	8.82	Tupputi.
Molybdenum ... ..	8.62	Bucholz.
Cadmium ... ..	8.694 to 8.604	Stromeyer.
Manganese ... ..	8.013	John.
Iron ... ..	7.844	Broling.
Indium ... ..	7.362	Winkler.
Tin ... ..	7.292	Kupffer.
Zinc ... ..	7.146	Wertheim.
Chromium ... ..	6.81	Wöhler.
Antimony ... ..	6.71	Marchand and Scheerer.
Tellurium ... ..	6.25	Berzelius.
Arsenicum ... ..	5.959 to 5.7	Guibourt.
Aluminum ... ..	2.67 to 2.56	Deville.
Strontium ... ..	2.54	Bunsen.
Glucinum ... ..	2.1	Debray.
Magnesium ... ..	1.743	Bunsen.
Calcium ... ..	1.578	Bunsen.
Rubidium ... ..	1.52	Bunsen.
Sodium ... ..	0.972	Gay-Lussac and Thénard.
Potassium ... ..	0.865	Gay-Lussac and Thénard.
Lithium ... ..	0.593	Bunsen.

(522) *Fusibility*.—The melting-points of the different metals differ not less widely than their densities. Mercury, for instance, remains fluid as low as  $-37^{\circ}.9$  ( $-38^{\circ}.8$  C.); potassium and sodium melt below the heat of boiling water. Tin, cadmium, bismuth, thallium, lead, and zinc melt below redness; antimony, calcium, and aluminum, above a red heat. Silver, copper, and gold require a bright cherry-red heat; iron, nickel, and cobalt a white heat; while platinum, iridium, rhodium, and several others, require the intense heat of the oxyhydrogen blowpipe, or even of the voltaic arc, to effect their fusion.

*Order of Fusibility of the Metals.*

Metal.	° C.	° F.	Observer.
Mercury ...	-38·8 ...	-37·9 ...	B. Stewart.
Rubidium ...	38·5 ...	101·3 ...	Bunsen.
Potassium ...	62·5 ...	144·5 ...	Bunsen.
Sodium ...	97·6 ...	207·7 ...	Regnault.
Lithium ...	180 ...	356 ...	Bunsen.
Tin ...	228 ...	442 ...	Crichton.
Cadmium ...	228 ...	442 ...	Stromeyer.
Bismuth ...	264 ...	507 ...	Rudberg.
Thallium ...	294 ...	561 ...	Crookes.
Lead ...	325 ...	617 ...	Rudberg.
Tellurium ...	} undetermined.		
Arsenicum ...			
Zinc ...	412 ...	773 ...	Daniell.
Antimony ...	about 1150 ...	621 ...	
Calcium ...	} above a red heat.		
Aluminum ...			
Silver ...	1023 ...	1873 ...	} Daniell.
Copper ...	1091 ...	1996 ...	
Gold ...	1102 ...	2016 ...	
Cast iron ...	1530 ...	2786 ...	
Cobalt ...	} highest heat of forge.		
Nickel ...			
Wrought iron			
Manganese	} agglomerate, but do not fuse in the forge.		
Molybdenum...			
Tungsten ...			
Chromium ...			
Palladium ...	} require the heat of the oxyhydrogen blowpipe.		
Platinum ...			
Rhodium ...			
Iridium ...			
Vanadium ...			
Ruthenium ...			
Osmium ...			

Some metals near their melting-points, before undergoing complete fusion, pass through a soft intermediate stage, in which, if two clean surfaces be presented to each other, and strong pressure or hammering be employed, they unite, or weld together, so as to form one continuous mass. Iron, thallium, lithium, and potassium afford the most striking instances of this. Palladium is also, in a minor degree, susceptible of it.

(523) *Volatility*.—Many of the metals admit of being volatilized without difficulty. Mercury, when heated under ordinary atmospheric pressure, boils, and is reduced to a perfectly colourless, transparent vapour, at about 662° (350° C.). It is important to observe that this dry vapour, though metallic, is an



insulator of electricity, and will allow the transmission of distinct electric sparks as readily as atmospheric air. The insulating power of mercurial vapour, on the one hand, and the small specific gravity of potassium, of sodium, and of lithium, on the other, show that there is nothing inconsistent with facts in the supposition that hydrogen itself, although the lightest known form of matter, and though gaseous, and consequently an insulator of electricity, may possibly be a metal; and indeed, in its chemical properties, it approximates very closely to this class of bodies. Eight of the metals are sufficiently volatile to be distilled from the compounds from which they are obtained, viz.,

Mercury	Zinc	Sodium
Arsenicum	Cadmium	Rubidium.
Tellurium	Potassium	

Arsenicum is volatilized below redness, and even before it has assumed the liquid form; cadmium requires a full red heat,  $1580^{\circ}$  ( $860^{\circ}$  C.), and zinc a temperature of  $1904^{\circ}$  ( $1040^{\circ}$  C.): whilst potassium, sodium, and rubidium require a still higher temperature. Those metals which are generally considered fixed in the fire are likewise volatilizable to a certain extent. In the process of lead-smelting, one-seventh of the lead escapes up the chimney, and would be wasted unless means for collecting it were adopted. Even copper is not absolutely fixed in the fire. My friend Dr. Percy, some years ago, showed me a remarkable illustration of this fact: he has in his possession part of a beam which, for many years, was suspended over a furnace in a copper smelting house in Norway; the whole beam, of which this is a fragment, contains minute beads of metallic copper studded through its texture: the copper must have been raised in vapour and so deposited within its fibres. Gold has been found similarly studding the beams of refineries; and it may be seen to undergo volatilization in the focus of an intensely powerful burning-glass. Platinum may be converted into vapour with scintillation in the oxyhydrogen jet, and silver has even been distilled in considerable quantities by Stas by the heat produced in the oxyhydrogen flame. Fine wires of the most refractory metals may be dispersed in vapour by transmitting the discharge of a powerful Leyden battery through them.

(524) *Conducting Power for Heat and Electricity*.—The great differences of expansion exhibited by different metals when exposed to equal degrees of temperature, have already been pointed out (132); and it may be stated generally that each metal possesses

a specific expansion ; the conducting power of each metal, both for heat (149) and for electricity is also definite (239, 276) ; in general, it is found that the best conductors of heat are also the best conductors of electricity ; but though conductors in the solid and liquid conditions, the metals are insulators in the aëriform state.

(525) ALLOYS.—Metals enter into combination with each other, and form compounds termed *alloys*, many of which are most extensively used in the arts. Comparatively few of the metals possess qualities such as render them suitable to be employed alone by the manufacturer ; aluminum, zinc, iron, tin, copper, lead, mercury, silver, gold, and platinum, constitute the entire number so used. Arsenicum, antimony, and bismuth are too brittle to be used alone, but are employed for hardening other metals. Many of the physical properties of the metals are greatly altered by combination with others ; the combination or alloy being often adapted to purposes for which either metal separately would be unfit.

Matthiessen has made a special study of the effects of alloying the metals upon their physical properties (*J. Chem. Soc.*, 1867, 201). He concludes that the metals may be divided into two principal classes in this relation : a small class, *A*, comprising lead, tin, zinc, and cadmium, which impart to their alloys their physical properties in the proportion in which they themselves exist in the alloy ; and a more numerous class, *B*, comprising most of the other metals.\* The members of the latter class do not impart to their alloys their physical properties in the proportion in which they themselves exist in the alloy.

The alloys which Matthiessen has examined consist of two metals. These he divides into three groups, viz. :—

- 1, Alloys formed by metals of the class *A* with each other ;
- 2, Alloys of metals of class *A* with those of class *B* ; and
- 3, Alloys of the metals of class *B* with each other.

Some of the physical properties of the metals are but little altered by alloying. The specific heat of the alloys and their expansion by heat are always the mean of that of their components ; and they vary as the proportions of each component vary. The specific gravity of the alloys of metals of class *A* is also the mean of that of their constituents ; but when metals of class *A* are alloyed with those of class *B*, the observed specific

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\* Probably brittle metals, like arsenic, antimony, and bismuth, should be excepted.

gravity is frequently a little above or below that which is given by calculation.

The fusing-point of an alloy is invariably below the mean of that of its components. In this respect, however, an alloy agrees with other mixtures; the chlorides when mixed with each other melt below the fusing-point of the mean, and often below the fusing-point of either constituent. The same thing is observed in mixtures of the carbonates with each other; it is also remarkably observed in the case of the silicates, as is well known both to the glass-maker and to the metallurgist: the latter avails himself of the fact to render his slags sufficiently fusible and liquid, by due admixture of various silicates.

A striking and well-known illustration of this increased fusibility of alloys is seen in what is known as *fusible metal*, an alloy of bismuth, lead, and tin. These metals, when melted together in the proportions of 4 parts of bismuth, 2 of lead, and 1 of tin, or nearly in the atomic proportion ( $\text{Bi}_2\text{PbSn}$ ), yield a mass fusible in boiling water, although the melting-point of tin, the most fusible of the three metals, is more than  $198^\circ$  ( $110^\circ \text{C.}$ ) higher, and that of lead is  $396^\circ$  ( $220^\circ \text{C.}$ ) higher; the easy fusibility of this alloy is always remarkable, even if the proportions of its constituents be considerably varied.

In the metals of class A, the conducting power for electricity is exactly proportional to the quantity of each metal employed, and the same thing is true as regards the conducting power of these alloys for heat; but when a metal of class B is alloyed either with one of its own class or with one of class A, a sudden decrease in conducting power both for electricity and for heat takes place.

Alterations in hardness and elasticity are still more easily perceived; and for many applications in the arts are of still greater importance. When a metal of class B is alloyed with a small proportion of one of class A, its elasticity is much increased. Bars of copper, of tin, of zinc, or of lead, when suspended and struck, emit a dead sound; but when bars of a copper-tin alloy (bell-metal) or of copper and zinc (brass) are struck, they emit a clear ringing sound. On the other hand, bars of tin-copper, with 12 per cent. of copper, or tin-lead, with 20 per cent. of lead, emit very little sound when struck; showing no marked change when the metals of class A are alloyed together, or when alloyed with a small proportion of a metal in class B. Similar results are observed when weights are suspended to spirals of hard-drawn wire: such spirals, if made of copper, silver, gold, or platinum,

become nearly straightened when stretched by a moderate weight ; but wires of equal dimension composed of copper-tin (12 per cent. tin), silver-platinum (30 per cent. platinum), and gold-copper (8·4 per cent. copper), scarcely undergo any permanent change in form when subjected to tension by the same weight. Many ductile metals belonging to class B are much increased in elasticity by being alloyed with each other.

Matthiessen gives the following approximative results upon the tenacity of certain metals and alloys for wires hard drawn through the same gauge (No. 23) :—

	lb.
Copper, breaking strain for double wire ...	25—30
Tin ... ..	under 7
Lead ... ..	" 7
Tin-lead (20 per cent. lead) ... ..	" 7
Tin-copper (12 per cent. copper) ... ..	about 7
Copper-tin (12 per cent. tin) ... ..	80—90
Gold ... ..	20—25
Gold-copper (8·4 per cent. copper) ... ..	70—75
Silver ... ..	45—50
Platinum ... ..	45—50
Silver-platinum (30 per cent. platinum) ...	75—80

Advantage is taken in the arts of this variation in the hardness and elasticity of metals produced by alloying them together.

Type-metal is an alloy of tin, lead, and antimony, which is fusible, expands at the moment of solidification so as to take the impression of the mould accurately, and is hard enough to resist wear without cutting the paper or being inconveniently brittle. The qualities of copper are also modified in an important manner by alloying it with other metals. Copper alone is not fit for castings, and it is too tough to be conveniently wrought in the lathe or by the file ; but when alloyed with zinc it forms a much harder compound, which can be cast, rolled, or turned, and which constitutes the different kinds of brass, the qualities of which can be varied by varying the proportions of the two metals. The addition of nickel to brass destroys its yellow colour, and produces the white compound metal known under the name of German silver. Copper and tin in various proportions yield the hard, tough, but moderately fusible compounds known as bronze and bell-metal.

When the metals combine with mercury, the resulting body is called an *amalgam*.

The ductility of metals is usually impaired by combination with one another. Alloys of two brittle metals are invariably brittle : such is the case with the compound of arsenicum and bis-

moth. Alloys of a brittle with a malleable metal are also brittle. Even when two malleable metals are united, the compound is sometimes brittle; gold, for example, when alloyed with a minute portion of lead, splits under the hammer. Generally speaking, the hardness of metals is increased by alloying them; of this a familiar instance is afforded by the standard coin of the realm: neither gold nor silver, when unalloyed, is sufficiently hard to resist attrition to the degree required for the currency, but the addition of one-tenth or one-twelfth of its weight of copper to either metal increases its hardness to the requisite extent.

In most cases these compounds of metals with each other are united by weak ties; for it appears to be necessary, in order to produce energetic union between any two bodies, that the substances when separate should exhibit great dissimilarity in properties. It has sometimes been questioned whether alloys are true chemical compounds: definite compounds of the metals with each other, do, however, certainly exist, and some have been found combined in definite proportions in the native state. Such is the case with silver and mercury, which occur crystallized together in the proportion of an atom of each ( $\text{AgHg}$ ). On forming alloys consisting of two metals only, it may be observed that if a solid metal be added to a melted metal, one of three different results may be obtained; either—1. The solid metal dissolves quickly with marked evolution of heat, as when gold is added to melted tin, or sodium to mercury: in these cases true chemical combination appears certainly to occur; 2. The solid metal dissolves quickly without any marked rise of temperature, as when lead is added to melted tin; or, 3. The metal dissolves slowly, as when copper is added to melted tin. In the last case the two metals separate partially on standing, so that it would appear that only a partial alloy is formed, each metal becoming dissolved only to a limited extent in the other, in the same manner as ether may to a certain extent be dissolved by water, and water to a certain extent by ether. Now, just as these two solutions may be mixed with each other, so may the alloys be mixed. Lead, for instance, will dissolve only 1.6 per cent. of zinc, and zinc 1.2 per cent. of lead. In like manner bismuth will dissolve 8.14 per cent. of zinc, and zinc 2.4 per cent. of bismuth.

Hence it appears that most alloys either are *mixtures* of definite compounds, with an excess of one or other metal, or they are *solutions* of the definite alloy in the excess of one of the metals employed, forming in their solid condition what Matthiessen calls a *solidified solution*. The separation of the components of

alloys from each other is sometimes easily effected by simple means. For instance, by exposing brass to a high temperature, the zinc is volatilized, leaving the copper behind; and, from the alloy of arsenicum and platinum, a heat sufficiently long continued will expel almost the whole of the arsenicum. Even mere mechanical means will sometimes suffice to effect the separation. When silver, for example, is amalgamated with mercury, the amalgam formed is dissolved by an excess of mercury: this excess, however, may be almost entirely removed by squeezing the mass through chamois leather; the amalgam is retained in the solid form, while the superfluous mercury, nearly freed from silver, escapes through the pores of the leather.

The chemical properties of an alloy are generally such as might have been anticipated from those of its components. In many instances, however, the alloy of two oxidizable metals is much more readily oxidized than either of its constituents. An alloy of 1 part of lead and 3 parts of tin, for example, burns when heated to dull redness much more easily than its components, and becomes converted into a white ash, used in the preparation of enamels (600). Sometimes an alloy is completely soluble in an acid which is without action upon one of its components:—German silver, which is a combination of copper with zinc and nickel, is readily dissolved by diluted sulphuric acid, though the acid will not attack metallic copper; and in a similar manner, an alloy of platinum with ten or twelve times its weight of silver is entirely dissolved by nitric acid, although platinum alone resists the action of the acid completely.

The more important alloys will, however, be best considered separately, when the individual metals which enter into their composition are described.

(526) *Condition in which the Metals occur in Nature.*—The ties which unite the components of an alloy are feeble, and are easily severed; but the compounds formed by the metals with the class of substances known as non-metallic, are for the most part held together by attractions of a very powerful order, and these compounds are in a chemical point of view much more interesting and important than the alloys. With some of the metals carbon and silicon combine in small proportion without appearing to destroy the metallic character; and, in fact, these compounds more resemble alloys than any other class of combinations: the most remarkable instances of carbides and silicides are furnished by iron, which, in its modifications of steel and cast iron, is combined with variable quantities of these elements. Many of the compounds of

the metals with sulphur preserve their metallic lustre, as is seen in galena and pyrites, yet lose nearly all the other physical properties by which the metals are recognized: ductility, malleability, and power of conducting electricity are extremely impaired. The metallic character is still more completely destroyed by oxygen, which converts the metals into bodies apparently earthy, as in the familiar cases of lime, magnesia, alumina, and zincic oxide; whilst chlorine and its allied group of elements form compounds which are most of them soluble, and possess all the qualities of true salts. The energy with which iron, zinc, and many other metals combine with oxygen is very remarkable: and the action of chlorine upon these metals is still stronger at ordinary temperatures.

The more common metals, on account of their powerful attraction for oxygen and sulphur, are very rarely met with in the uncombined form. Some of those which are less abundant are, however, found naturally in the metallic condition: such is the case with gold, silver, mercury, platinum, and copper. They are then said to occur in the *native state*. Many are found alloyed with each other; gold, for instance, forms native alloys with palladium and with silver; silver with mercury; antimony with arsenicum. The occurrence of native metals or natural alloys is, however, an exceptional circumstance, for the majority of the metals are found in combination with other elements. Oxygen and sulphur, in particular, from their powerful chemical attractions, and the abundance in which they occur, are the bodies most frequently associated with the metals; at other times arsenicum, and more rarely chlorine, are the mineralizing agents. These compounds, whether oxides, sulphides, arsenides, or chlorides, constitute what are termed the *ores* of the metals.

(527) *Distribution of the Metals*.—Next to silica in its various forms, the most abundant components of the rocks and superficial portions of the globe, are the compounds of lime, alumina, and magnesia. These earths are themselves oxides of metallic bodies, the attraction of which for oxygen is so intense that they are rarely isolated from it except for scientific purposes in the laboratory of the chemist. In their oxidized form they are everywhere scattered in abundance over the face of the globe. It is not so with those metals which man is in the habit of separating from their ores upon the large scale, and of employing for the various requirements of civilized society in the metallic state. Most of the ores of the highest importance and utility constitute but a comparatively small portion of the components of the earth's crust; but this deficiency in their relative proportion is more than compen-

sated by the mode of their distribution, for they are not dispersed at random, or diffused in minute quantity uniformly throughout the mass of the earth, but are collected into thin seams or beds, which form *mineral veins*.

Man has hitherto been able to penetrate but to a very small depth into the body of the earth, the deepest excavation which he has been enabled to make being not greater, in proportion to the diameter of the earth, than the thickness of an ordinary sheet of writing paper to a globe of two feet in diameter. Geological observations have shown, and any person who has traversed a railway cutting has had a partial opportunity of convincing himself of the fact, that a great part of the superficial portions of the globe consists of a succession of beds or layers—*strata*, as they are commonly termed—which rest one above another: these beds in some places retain nearly their original horizontal direction; but usually they have assumed a position more or less inclined, so as to form a considerable angle with the surface. The same stratum is liable to great variations in thickness in different parts, but each bed is found to occur in a uniform position in the series, the successive strata following each other in regular order, the uppermost being those of most recent formation. In this way the London clay rests upon the chalk, the chalk upon what is termed the green-sand, the green-sand upon the gault, and so on. The stratified or *sedimentary rocks* rest upon others, which, like granite, porphyry, and basalt, show no appearance of stratification, but bear marks, more or less evident, of having undergone igneous fusion.

Occasionally it happens that a thin bed of metallic ore forms a part of the regular succession of the strata: in Staffordshire, for instance, over many square miles of country, thin bands or seams of the ore termed clay iron-stone, varying in thickness from 5 to 20<sup>cm</sup>. (2 to 8 inches) are found lying between the beds of coal. Usually, however, the metalliferous masses occur in still older formations; such as in the mountain limestone of Cumberland and Derbyshire, or in the granite and clay-slate, as in Cornwall: they are then found in fissures which traverse the ordinary strata of the district, and assume a direction which, though it never becomes quite vertical, still approaches more or less towards this position. These fissures vary in thickness from a few centimetres to a metre or two: they are often filled with masses of basalt, granite, or trachyte (which have been injected from below, whilst the materials were in the molten state under the effects of subterranean heat), and then constitute what the miner terms *dykes*; but in other cases they are filled with metallic ores, and form mineral



veins or *lodes*. The ore sometimes occurs nearly pure ; at others mingled with quartz, fluor-spar, and various crystallized minerals, or else with earthy impurities of different descriptions. These veins extend from the surface downwards, often to a depth greater than can be followed even in the deepest mines. The veins which occur in the same district usually run in two directions, nearly at right angles to each other, the principal or original veins being traversed by the others. In Cornwall, for example, the metalliferous veins run nearly east and west, but they are occasionally intersected more or less obliquely by other lodes, to which the term of *caunter* (contrary) *lodes*, or *cross courses*, has been given.

These cross courses, however, are by no means always metalliferous ; they often appear to have been occasioned by the action of a force emanating from below, which, after bending and splitting the original strata, produced the fissures which were subsequently filled with quartz, clay, and various minerals. Such cross courses as these not seldom occasion the miner much trouble and perplexity, since the subterranean force necessary to produce them is often attended with great displacement of the original strata. A valuable vein of ore is from this cause frequently interrupted, and is sometimes lost altogether for want of knowing in what direction to seek for it. This sudden break in a vein and its displacement is, in mining language, termed a *fault*. It is very rarely that a single mineral vein occurs alone ; usually several are found together.

The thickness of the same vein, as might be expected, is subject to great variations ; at one time it dwindles to a mere thread, at others it attains considerable expansion. The most productive veins usually occur near the junction of two dissimilar kinds of rock—the metallic ores having probably accumulated there in consequence of slow voltaic actions which have been going on through uncounted ages, and which have been occasioned by differences in chemical composition of the two contiguous rocks : in Cornwall, for example, where so large a proportion of the mineral wealth of Great Britain is accumulated, the most important mines occur upon the junction of the granite with the clay-slate or *killas*.

(528) *Mining Operations*.—The existence of a vein having been ascertained, and its *dip*\* or inclination to the horizon, and

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\* The terms *dip* and *strike* have been illustrated by the roofs of a row of houses running east and west ; the ridge pole shows the direction of the strike of the strata east and west, whilst the slope of the slates shows the dip to the north and to the south.

general direction or *strike* having been determined, the miner commences by sinking a vertical pit or *shaft*, in such a manner that he calculates upon cutting through the lode at some 30 or 40 fathoms (from about 50 to 70 metres) below the surface. When he has reached the lode, he *drives* a gallery, or *level*, horizontally into it, right and left, raising the ore to the surface through the shaft. If the produce be such as to encourage him to proceed, a second shaft is sunk in the course of the lode, at the distance of about 100 yards or 90 metres from the first, and into this the gallery or level is driven, so as to facilitate the ventilation of the mine and the extraction of the ore. In order to be able to remove the ore from other parts of the lode above and below the point at which the first level is made, the shaft is continued downwards, and other galleries, or *cross cuts*, as they are termed, are made, both above and below the first level, at intervals of ten fathoms (about 18 metres), to meet the lode at different points; these cross cuts are at right angles to the levels.

Fig. 332 shows a vertical cross section of the lode at the Callington Mine. *E S* represents the engine shaft, *V V* the vein or lode, and *c, c*, the cross cuts.

FIG. 332.

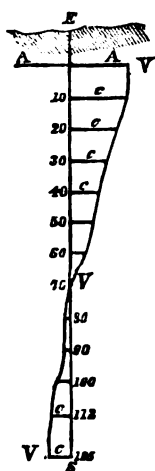


FIG. 333.

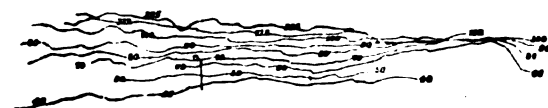
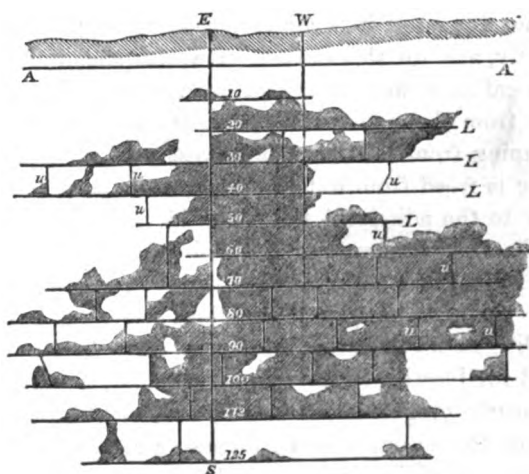


FIG. 334.

The levels cannot be shown in this view; but whenever a cross cut meets the lode, a level is driven east and west, in the direction of the lode itself.

II.

Y

Fig. 333 shows the arrangement of the levels in the same mine; *E s* represents the engine shaft, *w*, a second smaller shaft, and *L, L, L*, the different levels, the depths of which in fathoms are indicated by the numbers attached to them; these levels communicate at different points by short cuts, or *winzes*, as the Cornish miners term them; they are shown at *u, u*, in various parts, and are needed to facilitate the extraction of the ore from different parts of the lode. The different levels are not immediately over, or parallel to each other, but their direction and position varies with that of the inclination and direction of the lode. This is explained by fig. 334, in which the direction of these galleries is exhibited; it represents a *plan* of the mine, supposing the figures to refer to the levels shown in 333: the lode, it will be seen, does not preserve the same dip at all points, being much more nearly vertical at the right than at the left extremity of the plan. The cross cuts cannot be shown in fig. 333. The shaded parts in this figure indicate the portions of the lode which have been already worked away. The galleries in the mine are supported by strong timbering, the object of which is to prevent the rubbish from falling in and overwhelming the men while engaged in their work.

One of the principal difficulties which the miner has to contend with is the continual oozing of water into the mine in all directions. Where the mine, as very often happens, is situated upon the side of a hill, an *adit level*, or watercourse, shown at *A, A*, fig. 333, is carried from the shaft to the lowest accessible point of the surface; and through this the waters of the upper part of the mine readily escape; but when the workings extend below this point it becomes necessary to pump more or less constantly, and for this purpose powerful steam-engines are required. The galleries and levels are so constructed that the water shall flow from them into the principal shaft of the mine, so that by pumping from the *sump*, or lowest part of this shaft, the whole mine is freed from water. The greater part of the water is lifted only to the adit level, but a considerable quantity is raised to the surface for the purpose of washing the ore.

Much of the excavation is done by hand, with the pickaxe and wedges; but after judicious clearing, gunpowder properly applied facilitates the progress greatly. The quantities of powder used for blasting in the mines are small, usually about two ounces, or nearly 57 grammes. The process of blasting consists in boring a hole to the depth of 18 inches or 2 feet (45 or 60 centimetres), somewhat obliquely, under the portion of rock which is to be raised; the powder is then introduced, and the hole is closed by ramming in clay or friable rock. A copper wire runs from the surface down to the charge, and when the ramming or *tamping* is finished, the wire is withdrawn and its place supplied with a hollow rush charged with powder, and the train is fired by means of a fusee. A safety fusee is now commonly substituted for the copper wire and pithed reed filled with powder; and in hard rocks

gun-cotton may advantageously be substituted for gunpowder. The ore that is detached is raised to the surface of the mine in large wrought-iron buckets, or *kibbles*, which are capable of containing about 3 cwt. of ore.

(529) *Mechanical Treatment of the Ores.*—The extraction of metals from their ores is effected by two classes of operations; those of the first class are mechanical; by their means the earthy parts contained in the matrix or vein-stone are to a certain extent separated: the operations of the second class are chemical, by which the metal itself is procured. The mechanical treatment is influenced not only by the nature and composition of the ore, but also by its market value: an ore of tin, of copper, or of lead, from the higher price which the metal bears, will be worth a more elaborate treatment than an ore of iron or of zinc.

The ores of zinc and of iron are occasionally subjected to the operation of washing; for when they are accompanied by a loose friable clay, the clay admits of being readily diffused in a finely divided state through the water, and is easily removed by its means. The specific gravity of clay is not much more than 2·0, whilst that of ferrous carbonate and hydrated ferric oxide varies from 3·8 to 4·0, and that of calamine is about 4·2; consequently particles of these materials of equal size expose a smaller surface in proportion to their weight to the action of water than the clay, and when agitated with water they subside more rapidly; and if subjected to the action of a current of water, they are held for a shorter time in suspension, and are therefore carried by it to a smaller distance.

The same principles apply to the more elaborate processes of washing adopted with the ores of lead and tin. Galena has a specific gravity of 7·6; tinstone of about 7. Baric sulphate has a density of 4·6; fluor-spar of 3·1; and quartz of 2·65. When reduced to particles tolerably uniform in size, the earthy portions may therefore to a considerable extent be separated, by the action of water, from the ores of lead and tin.

The following is an outline of the mechanical operations pursued in *dressing* the ores of lead and tin; and the same method is to a certain extent adopted with the copper ores:—

The ore having been brought to the surface, if a lead or copper ore, is first sorted by hand: the purest portions, or *prills*, as the Cornish miners term them, are set aside, and are ready for smelting without further preparation; but the bulk of the ore is broken by hammers into lumps of about the size of a walnut, and the best pieces are again picked out by hand. The rougher portions go to

the crushing mill, which consists of a pair of horizontal cylinders placed parallel to each other at a little distance apart: the cylinders may be either grooved or plain. The ore is supplied to them by a hopper from above. After passing through the mill, the crushed ore is sifted through coarse sieves; the coarser parts are set aside for the stampers, and the finer portion is subjected to the operation of *jigging*. This consists in plunging the ore contained in a sieve into a pit, through which water is constantly flowing: the workman keeps the ore in continual agitation, alternately raising and lowering the sieve, to which he also gives an alternate rotatory motion, taking care always to keep it beneath the surface of the water. By this means, the contents of the sieve are separated into layers of different quality. If it be a lead ore which is undergoing treatment, the galena, from its friable character, is easily reduced to small fragments: most of the galena, therefore, passes through the sieve and subsides to the bottom of the pit, whilst what is left upon the sieve consists chiefly of the less friable fluor-spar and quartz. This residue is mixed with the inferior qualities of ore, and is transferred to the stamping mill, whilst the richer part is set aside for smelting.

Tin ore is usually disseminated through a compact hard matrix, and passes at once to the stampers.

The stamping mill consists of five or six upright wooden beams, the lower ends of which are shod with iron, each beam weighing about  $2\frac{1}{2}$  cwt. These are placed in a wooden frame, and are alternately lifted up and allowed to fall back upon the ore by the action of arms projecting from a horizontal axle, which is turned by water or steam power. The ore is placed on an inclined plane behind the stampers, and slides down under them, and is crushed. The crushed particles, when reduced to a sufficient degree of fineness, are washed out through a grating in front, by the action of a current of water which is constantly flowing through the mill: the washed ore is carried into a channel in which two pits are formed; in the one nearest the mill the purer and heavier part of the ore, or *crop*, is deposited; whilst the more finely divided portion, technically termed *slime*, or *schlich*, accumulates in the second.

The crushed ore now undergoes a series of washings, the object of which is to separate the impurities from the valuable part of the ore.

The crop is first subjected to washing in the *buddle*; this is a wooden trough, fig. 335, nearly 2.5 metres long, 1 metre wide, and 0<sup>m</sup>.6 deep, or about 8 feet long, 3 wide, and 2 deep, fixed in the ground, with one end somewhat elevated. At the upper end, a small stream of water enters, and is reduced to a uniform

thin sheet by means of a distributing board, *a*, on which a number of small pieces of wood are fastened to break the stream. The ore to be washed is placed in small quantities at a time upon a board, *b*, somewhat more inclined than the body of the buddle, and it is spread out into a thin layer; the water carries it forward: the richer portions subside near the head of the trough, and the lighter ones are carried further down. "The heads" are then tossed in the *kieve*, or tub, shown at *c*, which is filled with water, and ore added by a workman, who keeps the contents of the kieve in continual agitation by turning the paddle or agitator, the handle of which is seen projecting at the top. When the vessel is nearly full, the agitation is stopped—the kieve is struck smartly upon the side several times, and its contents are allowed to subside; the upper half of the sediment is again passed through the buddle. Various modifications of the washing process are resorted to, but they are all the same in principle.

FIG. 335.



A rough estimate of the value of any sample of dressed ore is obtained by the process called *vanning*:—A small quantity of the ore is placed on a shovel, and agitated gently with a peculiar circular movement in water, then, by giving it a dexterous lateral shake, the different constituents arrange themselves according to their density—the galena, or the tin-stone, at the bottom; above this are iron pyrites and blende; and at the top are the fluor-spar and quartz. The eye then at a glance roughly estimates the quantity of each.

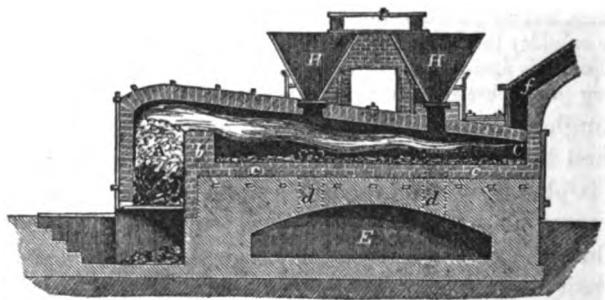
The water employed in the various washings is not allowed at once to run to waste, but is made to pass through a long shallow channel, in which the slime and mud which have been carried away in the different operations may subside. This slime still retains some portion of ore; and in order to recover this as far as possible, it is again subjected to the action of a fine stream of water, either upon an inclined table, which acts in a manner similar to the buddle,—or it is washed upon a swinging table, the bed of which is also inclined, but moveable, and is suspended by chains from supports at the four corners; the bed is alternately thrust forward 2 or 3 inches (about 6 or 8 centimetres) by the revolution of a cam-wheel, and is then allowed to fall back against solid wooden bearings with a sudden jar. The ore is spread upon a board which overhangs the upper part of this

table, and is carried forward by a gentle stream of water; the heavier particles of the ore, owing to the superior momentum which their density gives them, are by this jarring movement of the table carried back to the upper part of it, whilst the lighter impurities are washed away.

(530) *Roasting, or Oxidation.*—The chemical operations are divisible into two main branches, one dependent on the addition, the other on the removal of oxygen. If the mineral contain volatile ingredients, such as sulphur or arsenicum, the process of *roasting*, or oxidation, is first resorted to. In principle it is very simple; the mode of effecting it varies, however, in different cases. In the most common method, a furnace of particular construction, termed a *reverberatory*, is employed.

Fig. 336 shows a section of a reverberatory furnace, such as is employed for roasting copper ores; *t* is the platform, from which the hoppers, *H, H*, are

FIG. 336.



charged with the ore, which at proper intervals is allowed to fall upon the bed, *c c*: the fuel is consumed upon a distinct hearth, *a*, and does not come into contact with the ore, from which it is separated by the bridge, *b*: the heated gases, as they arise from the burning mass, are, from the construction of the arched roof, reverberated, or driven down upon the ore to be roasted, and then pass off through the flue *f*: when sufficiently roasted, the ore is allowed to fall into the arched recess, *x*, beneath the bed of the furnace through openings, *d, d*, which are kept closed by sliding plates till the roasting is complete.

After the fire has been lighted, a constant supply of air to the mineral is maintained, and care is taken to prevent the heat from rising so high as to melt the ore, which is stirred at intervals to expose fresh surfaces to the action of the air: the sulphur burns off in the shape of sulphurous anhydride, which escapes into the atmosphere, whilst the arsenicum forms arsenious anhydride; most of this, though volatile, speedily becomes condensed, and is collected on the sides of the chimney, or else in chambers constructed for its reception, whence it is removed at intervals, and subsequently purified. In metallurgic operations where sul-

phides of metals of different degrees of oxidability are present, it may happen that the sulphide of the more oxidizable metal is completely converted into a metallic oxide, whilst sulphurous anhydride escapes, and that the sulphide of the less oxidizable metal is reduced to the metallic state. For example, in roasting copper pyrites (the double sulphide of copper and iron), the iron is wholly converted into oxide, whilst the copper is extracted at once in the metallic state, by a series of careful roastings (870). In the case of plumbic sulphide, where the metal possesses but a moderate degree of oxidability, it is also the practice so to regulate the supply of air in the furnace that the sulphur is wholly expelled in the oxidized condition, whilst the greater part of the lead is extracted in the form of metal during a single roasting in the reverberatory (890). Where the metal possesses a high degree of oxidability, as is the case with zinc, it is not practicable to limit the degree of oxidation in this manner during the roasting: the metal itself passes into the state of oxide, simultaneously with the expulsion of the sulphur as sulphurous anhydride (702).

(531) *Reduction, or Smelting.*—The second chemical process for the extraction of the metals, that of *reduction*, is applicable to most metallic oxides, whether of natural or of artificial origin. The object in this case is to remove the oxygen, by presenting to the mineral some body which, at a high temperature, has a stronger attraction for oxygen than the metal itself possesses. The furnaces employed in this operation are often of great size, and vary in form with the nature of the metal: in them the ore is heated intensely, in contact with carbon; carbonic oxide and carbonic anhydride are thus produced, and from their gaseous nature are quickly removed from the sphere of action. It becomes necessary at this stage to get rid completely of the earthy and other impurities of the ore, which the mechanical operations never succeed in removing entirely, and which often form a large proportion of the ore. In order to effect this, certain fluxes, or substances capable of forming fusible compounds with the earthy matters, are added at the same time with the carbon; these melt and form a kind of glass, through which the reduced metal, from its superior density, sinks, and is thus completely defended from contact with the air: the metal is at suitable intervals drawn off from the bottom of the furnace, while the melted glass—or *slag*, as it is termed—runs off at an aperture left in the side for the purpose. Limestone is in some cases added to the ore with the view of aiding the fusion of the siliceous impurities: in other instances fluor-



spar or some other readily fusible material is added, for the purpose of increasing the fluidity of the slag. Much judgment is required in the selection of the flux, and in deciding upon the proper proportion to be added: frequently this object is economically effected by a judicious mixture of different ores of the same metal, each of which aids the other by supplying some compound which was wanting to render the slag sufficiently fusible.

The various modifications of these processes will be described as they present themselves in connexion with the different metals which require these modifications. Other modes of separating individual metals are employed, which will be alluded to in their respective places. For details upon metallurgic processes, Percy's *Metallurgy*, or the fourth volume of Dumas' valuable work, *Traité de Chimie appliquée aux Arts*, may be consulted; and the second and third volumes of the same work contain many excellent descriptions of processes in which metallic chemistry is applied to the purposes of industry and commerce. Phillips's *Metallurgy* is a smaller and more compendious treatise on this subject.

(532) *Classification of the Metals*.—The metals may be divided into eight groups (page 12), regard being principally had in this arrangement to the convenience of indicating the method of testing for the presence of the metal, in the ordinary processes of analysis; in consequence of which it is sometimes necessary to depart from the strictly natural order.

In treating of the groups of the non-metallic and electronegative elements, it has been remarked that the electronegative character of those belonging to the same group is most strongly marked in those which have the lowest combining number; chlorine, for example, being more active than bromine, and bromine than iodine. With the basylous or electropositive elements, the reverse generally holds good; the basic power of rubidium, for example, being greater than that of potassium, that of potassium greater than that of sodium, and that of sodium being superior to the basic power of lithium.

I. The metals of the alkalis; these are five in number—viz.,

1. Potassium	3. Lithium	5. Rubidium.
2. Sodium	4. Cæsium	

These metals present a close analogy in properties; sodium, which is intermediate in properties between potassium and lithium, possesses a combining number which is the arithmetic mean of the two; for  $\frac{39+7}{2}=23$ . In like manner the atomic

weight of rubidium (85.3) is intermediate between that of cæsium and potassium  $\frac{133+86}{2}=86$ . A similar remark is applicable to the intermediate member of some of the other groups.

The corresponding salts formed by the metals of the alkaline group are isomorphous only when they contain equal atomic proportions of water of crystallization. With these metals will be described the salts of ammonium: they are isomorphous with the salts of potassium, and indeed present the closest analogy with them.

The metals of the alkalis are distinguished by the following characters:—They are monad or uniequivalent, and therefore displace 1 atom of hydrogen from the acids. They are soft, easily fusible, and volatile at high temperatures: they have an intense attraction for oxygen, and become tarnished immediately that they are exposed to the air; when thrown upon water they decompose it at all temperatures with rapid disengagement of hydrogen: they each form at least two oxides, but only one of these, that with the smallest proportion of oxygen, forms salts: the general formula of this basic oxide is  $M_2O$ . These basic oxides combine with water with great avidity, yielding soluble hydrates of the general formula  $MHO$ ; their aqueous solutions are powerfully caustic and alkaline. When they have once combined with water, the compound thus obtained cannot be rendered anhydrous by heat alone. In these metals the basylous quality, or their capacity for saturating the acids, is developed to the highest degree. The hydrated alkalis, when exposed to the air, either in the solid form or in solution, absorb carbonic acid rapidly: each alkali forms with this acid two salts, a normal carbonate, and an acid carbonate commonly known as the bicarbonate, both of which are freely soluble in water. The metals of the alkalis combine with sulphur in several proportions; all of these compounds, also, are soluble. With chlorine they form but a single chloride; but their oxides have the power of combining with chlorine, and forming compounds possessed of bleaching properties. Lithium, from the sparing solubility of its carbonate, furnishes the connecting link between this group and the one which follows it.

II. The metals of the alkaline earths are three in number—viz.,

1. Barium      |      2. Strontium      |      3. Calcium.

These metals are dyad, 1 atom usually displacing 2 atoms of hydrogen from its combinations. They decompose water at all temperatures with great rapidity; with the exception of barium, they each form only one oxide, and this oxide combines with water

with avidity, but the hydrate so formed, with the exception of that of barium, may be decomposed by ignition. The hydrated oxide is soluble to a certain extent in water, and is capable of forming salts by its reaction upon acids. They each furnish but one chloride, which assumes the form of  $N''Cl_3$ . The metals of this group are also powerfully basylous. They form several sulphides which are soluble in water, the protosulphides being less so than those which contain higher proportions of sulphur. With chlorine their oxides form bleaching compounds. Their carbonates are insoluble in pure water, but are soluble to a small extent in water charged with carbonic acid. They form insoluble phosphates and oxalates. The corresponding salts of these metals are in many cases isomorphous.

III. Metals of the earths : eight in number—viz.,

1. Aluminum	4. Erbium	7. Lanthanum
2. Glucinum	5. Terbium	8. Didymium.
3. Yttrium	6. Cerium	

The oxides of this class are insoluble in water ; some of them are dissolved by solutions either of the caustic alkalies or of their carbonates. The phosphates of this group are insoluble in water. Aluminum and glucinum do not decompose water at ordinary temperatures unless the metals are in a very finely divided state : the other metals of this group are scarcely known in an isolated form, and their analogies are but ill-defined. The oxides of cerium, lanthanum, and didymium, are more or less coloured ; those of the other metals are white. The basylous character of this group of metals is much less marked than that of the preceding ones. When salts of these metals in solution are mixed with ammoniac hydrosulphide, precipitates consisting of hydrated oxides instead of sulphides are formed, whilst sulphuretted hydrogen escapes. Many of these metals are very rare, and their properties have been but imperfectly examined. Aluminum, by the isomorphism of its oxide with ferric oxide, the volatility of its chloride, its slight attraction for carbonic acid, and other peculiarities, connects this group with the group of iron metals.

IV. Magnesian metals, three in number :—

1. Magnesium	2. Zinc	3. Cadmium.
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Magnesium is usually reckoned as one of the metals of the alkaline earths ; but from its power of resisting oxidation at the ordinary temperature of the air, its volatility at high temperatures, the isomorphism of its salts with those of zinc, the sparing solubility of its oxide and its sulphide, the solubility of its sulphate,

and several other particulars, it stands in closer relation to zinc and cadmium. Magnesium, zinc, and cadmium are dyads; they all burn with flame when heated in air to a sufficiently high temperature, and each of these metals forms but a single oxide, chloride, and sulphide, as well as but a single class of salts with the radicles of the acids.

V. Metals more or less analogous to iron; six in number:—

1. Cobalt		4. Iron
2. Nickel		5. Chromium
3. Uranium		6. Manganese.

They all act in combination as dyads in one series of their compounds, but many of them are triad in another series. These metals, when heated to dull redness, decompose the vapour of water if it be transmitted over them, and become converted into oxides, whilst hydrogen escapes: they are also soluble with effervescence and evolution of hydrogen in diluted sulphuric or in hydrochloric acid. The protoxides of the metals of this class are powerful bases: they have the general formula  $N''O$ . They yield hydrates, usually of the form  $N''O, H_2O$ , and lose their water readily when heated. These protoxides, with the exception of that of uranium, are dissolved more or less freely by ammonia, especially if ammoniac chloride be present in the solution. Each of the metals of this group forms a sesquioxide, which, excepting in the case of those of cobalt and nickel, reacts with acids and forms corresponding salts: they also form an oxide of the form  $NO, N_2O_3$ , corresponding with the magnetic oxide of iron ( $FeO, Fe_2O_3$ ). Several of the metals of this group—viz., iron, chromium, and manganese—form trioxides or even higher oxides, which are very soluble in water, and furnish powerful metallic acids. Hydrated sulphides of these metals are produced by the addition of a solution of sulphide of potassium or of ammonium to a solution of their salts; the precipitate so occasioned is insoluble in excess of the alkaline sulphide. The chromic salts, however, are precipitated as hydrated chromic sesquioxide, not as sesquisulphide. Sulphuretted hydrogen gas, when transmitted through the solutions of these metals acidulated with sulphuric acid, occasions no precipitate of sulphide, excepting in the case of the salts of cadmium. Corresponding salts furnished by the protoxides of this group are isomorphous: and the salts formed by the sesquioxides with the same acid are likewise isomorphous with each other. Chromium and manganese also exhibit an isomorphous relation to the sulphur group, inasmuch as the correspond-

ing sulphates, chromates, and manganates have the same crystalline form. In the case of manganese a singular connexion with the halogens is exhibited in the isomorphism of the permanganates with the corresponding perchlorates and periodates.

VI. Metals which yield acids when their higher oxides are combined with water; of these there are twelve, as follow :—viz.,

1. Tin	5. Molybdenum	9. Vanadium
2. Titanium	6. Tungsten	10. Arsenicum
3. Zirconium	7. Niobium	11. Antimony
4. Thorium	8. Tantalum	12. Bismuth.

The first four of these metals are biequivalent or dyads under certain circumstances, but tetrad or quadreequivalent in other more usual cases; the next three are sometimes tetrads, but often hexads, or equivalent to six atoms of hydrogen; the three which follow are pentad; whilst the last three, though usually triads, are occasionally, as in pentachloride of antimony, pentad or quinqueequivalent.

A close parallelism in properties exists between tin and titanium, corresponding compounds such as tinstone ( $\text{SnO}_2$ ) and rutile ( $\text{TiO}_2$ ) being isomorphous; each yields a liquid volatile tetrachloride, and in this particular, as well as in their powerful attraction for fluorine, they exhibit considerable analogy with silicon: zirconium and thorium are similarly related to each other and to silicon, they furnish a dioxide; whilst niobium, and tantalum, according to Marignac, and vanadium, according to the recent researches of Roscoe, all furnish an anhydride with 2 atoms of the metal and 5 atoms of oxygen, form a volatile pentachloride, and yield definite compounds with fluorine. Molybdenum and tungsten, have likewise strong analogies with each other.

Stannous oxide is a powerful base; but basic qualities are nearly wanting in the oxides of the other metals in this group. The metals included in this class decompose water when its vapour is driven over them at a red heat (with the exception of arsenicum, which is more allied in character to phosphorus than to the metals): but they do not evolve hydrogen when treated with diluted sulphuric acid, owing to their want of basylous power. Many of them, owing to this tendency to form acids, decompose water with evolution of hydrogen in the presence of a powerful base, such as potash. The metallic acids formed by these metals are, with the exception of arsenic acid, nearly insoluble in water. The persulphides of this group of metals are soluble in the sul-

phides of the alkali-metals, and in many cases form crystallizable compounds with them.

VII. The next group contains four metals :—viz.,

- |           |  |         |  |             |  |            |
|-----------|--|---------|--|-------------|--|------------|
| 1. Copper |  | 2. Lead |  | 3. Thallium |  | 4. Indium. |
|-----------|--|---------|--|-------------|--|------------|

They are not related to each other by any strong chemical resemblances ; copper and lead exert no decomposing action upon water, even at a full red heat ; all form powerfully basic oxides. Copper and lead exhibit a considerable tendency to the formation of basic salts : they are not dissolved by either diluted sulphuric or hydrochloric acid ; they are precipitated from acid solutions by sulphuretted hydrogen, and their sulphides do not combine with the sulphides of the alkali-metals, but in the case of thallium the precipitation is incomplete. Copper forms salts which are isomorphous with those derived from the protoxides of the metals in the iron group, and in the compounds which it forms with carbonic acid, displays a close correspondence with magnesium and zinc, as well as with cobalt and nickel ; and lead in some of its compounds is isomorphous with those of the alkaline earths, but in chemical properties it is more allied to mercury and silver ; whilst in some organo-metallic compounds it has tetrad powers. Thallium is usually monad, occasionally triad ; copper is occasionally monad, as in the cupreous chloride, but in the majority of cases it, like lead, is dyad in function.

VIII. The last group consists of the noble metals, of which there are nine—viz.,

- |            |  |              |  |              |
|------------|--|--------------|--|--------------|
| 1. Mercury |  | 4. Platinum  |  | 7. Ruthenium |
| 2. Silver  |  | 5. Palladium |  | 8. Osmium    |
| 3. Gold    |  | 6. Rhodium   |  | 9. Iridium.  |

These metals are unable to decompose water at any temperature. They have but a feeble attraction for oxygen ; the oxides of the first five are decomposed by simply heating them to a temperature below a visible red, the metal remaining in an uncombined form ; and in many cases simple exposure to a strong light produces a similar decomposition ; all of them yield more than one series of salts. Mercury and silver are often found mineralized in the form of sulphides, but the other metals of this group usually occur in the native state, several of them being frequently associated together. Their attraction for sulphur and for chlorine is much stronger than for oxygen. All of them form at least two chlorides, and some three or even four : the chlorides of the noble metals have a strong tendency to form double chlorides with the chlorides of the metals of the alkalis.

Silver exhibits considerable analogy with lead: it is powerfully basylous; palladium is somewhat allied to copper.

## § II. GENERAL PROPERTIES OF THE COMPOUNDS OF THE METALS WITH THE NON-METALLIC ELEMENTS.

(533) **THE OXIDES.**—The most important compounds of the metals with the non-metallic bodies are those which they form with oxygen. The oxides in many cases constitute abundant and valuable metallic ores; such as the different forms of hæmatite, the specular and magnetic iron ores, and tinstone, the ordinary ore of tin.

The metallic oxides may be subdivided according to their chemical functions into 3 classes:—viz., 1, basic oxides; 2, saline or indifferent oxides; and 3, metallic anhydrides, which when hydrated form the metallic acids.

The atomic proportions in which the constituents of the principal varieties of metallic oxides are united are exhibited in the following table:—

1. *Suboxides*, „N<sub>2</sub>O,\* of the type H<sub>2</sub>O; feebly basic, such as—  
Cupreous oxide „Cu<sub>2</sub>O.
2. *Monoxides*† M'O or N'O, of the type H<sub>2</sub>O; strongly basic, such as—  
Argentio oxide, Ag'<sub>2</sub>O | Lime, Ca''O.

\* When the atom of a dyad enters into combination with powers equivalent only to those of the atom of a monad, the fact may be indicated as in the text, by placing two dashes at the bottom and to the left of the symbol.

† These oxides may, in fact, be regarded as compounds formed upon the type of a single atom of water, HHO, if each atom of hydrogen in the molecule is displaced by an atom of a metallic monad, such as potassium; or if both atoms of hydrogen be displaced by a single atom of a metallic dyad, such as barium, we have an analogous oxide; for example:—

HHO, water,  
KKO, anhydrous potash,  
Ba''O, anhydrous baryta;

but if only one atom of hydrogen be displaced by the metallic monad we have a hydrate of the metallic oxide. If the metallic dyad displaces half the hydrogen of two atoms of water, we have a hydrate of the oxide of the metallic dyad, as for instance:—

$\left. \begin{matrix} K \\ H \end{matrix} \right\} O$ , potassic hydrate ;  $\left. \begin{matrix} H \\ Ba'' \\ H \end{matrix} \right\} O$ , baric hydrate.

In the sesquioxides and trioxides the *molecular* type is a group consisting of three atoms of water, each atom of the metal representing 3 or 6 atoms of

3. *Sesquioxides*,  $N'''_2O_3$ , of the type  $H_6O_3$ ; feebly basic, neutral, or even acid, such as—

Alumina,	$Al'''_2O_3$
Uranic sesquioxide,	$U_2O_3$
Cobaltic sesquioxide,	$Co'''_2O_3$
Arsenious sesquioxide,	$As'''_2O_3$

4. Three-fourths oxides,  $N_3O_4$ , of the type  $H_8O_4$ : saline oxides, such as—

Magnetic oxide of iron,	$Fe''Fe'''_2O_4$ , or $Fe''O, Fe'''_2O_3$
Chrome ironstone,	$Fe''O, Cr'''_2O_3$

5. *Dioxides*,  $N^IV_2O_2$ , of the type  $H_4O_2$ ; rarely basic, but generally neutral or acid, such as—

Platinic dioxide,	$Pt^IV_2O_2$
Baric dioxide,	$BaO_2$
Stannic dioxide,	$Sn^IV_2O_2$

6. *Trioxides*,  $N^VI_2O_3$ , of the type  $H_6O_3$ ; metallic anhydrides, such as—

Molybdic trioxide,	$Mo^VI_2O_3$
Tungstic trioxide,	$W^VI_2O_3$

7. *Anhydrides*,  $R^V_2O_5$ , of the type  $H_{10}O_5$ —

Arsenic anhydride,	$As_2O_5$
Antimonic anhydride,	$Sb_2O_5$

The oxides constitute so important a series of compounds, that it will be necessary to consider their relations, particularly to water and to the acids, somewhat more in detail, classifying them in the order just indicated.

1. *Suboxides*, of the type „ $N_2O$ .—A few of the dyad metals, such as copper, lead, and mercury, form oxides in which one atom of the metal, which usually is equivalent to *two* atoms of hydrogen, becomes for the time equivalent only to a single atom of hydrogen. For example, we have the cupreous oxide, or red oxide of copper ( $Cu_2O$ ); mercurous oxide, or black oxide of mercury ( $Hg_2O$ ); and plumbous oxide ( $Pb_2O$ ). Though these oxides usually give rise to an unstable series of salts, they frequently become decomposed into the normal oxide and free metal; cupreous oxide, for instance, becoming converted into metallic

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hydrogen in the combination; alumina being  $(Al''')_2O_3$ , and its normal hydrate  $Al'''H_2O_5$ .

The dioxides correspond in composition to a group containing 2 atoms of water; the  $\frac{3}{2}$  oxides to a group containing 4 atoms of water, and so on, as indicated in the table.



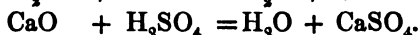
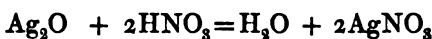
copper and the black oxide;  $\text{Cu}_2\text{O} = \text{Cu} + \text{CuO}$ ; but with hydrochloric acid the reaction is as follows:  $\text{Cu}_2\text{O} + 2\text{HCl} = \text{H}_2\text{O} + \text{Cu}_2\text{Cl}_2$ . No normal hydrates of these oxides appear to exist, the mercurous and plumbous oxide being anhydrous, and the yellow hydrated cupreous oxide being  $4\text{Cu}_2\text{O}, \text{H}_2\text{O}$ , instead of  $\text{CuHO}$ .

2. *Monoxides*, of the type  $\text{M}'_2\text{O}$ , or  $\text{N}''\text{O}$ .—This class of oxides includes all the most powerful bases: they are formed by the union either of 2 atoms of a metallic monad with 1 atom of oxygen, or by the union of 1 atom of a metallic dyad and 1 of oxygen. The first subdivision includes the five alkalis and the oxides of thallium and silver. Among the members of the second subdivision are included the alkaline earths, the oxides of lanthanum, didymium, magnesium, zinc, and cadmium, and the protoxides of cerium, uranium, cobalt, nickel, iron, chromium, manganese, tin, copper, lead, mercury, and palladium. The anhydrous oxides of the alkali-metals become converted into hydrates with extrication of intense heat on the addition of water, which dissolves them rapidly and in large quantity; one atom of water and one of alkali yielding two atoms of the hydrate: *e.g.*,  $\text{KCO} + \text{HHO} = 2\text{KHO}$ . The hydrates of the alkalis cannot be again decomposed by exposure to heat, but are slowly volatilized without decomposition by a prolonged elevation of temperature. Hydrated argentic oxide is very unstable; it is soluble only in a very slight degree.

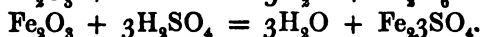
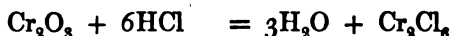
The action of water upon anhydrous baryta, strontia, and lime is also very energetic, a single atom of the hydrate being in each case formed by the combination of single atoms of water and the earth: as, for instance,  $\text{CaO} + \text{H}_2\text{O} = \text{CaH}_2\text{O}_2$ . Calcic hydrate requires a full red heat for its decomposition, but the hydrates of baryta and strontia fuse at an elevated temperature, and baric hydrate does not part with water, even by prolonged ignition. These hydrates are soluble in water, though that of lime is but sparingly so. Magnesia combines very slowly with water. It is very sparingly soluble; plumbic and mercuric oxide are each somewhat more soluble. The other oxides above enumerated do not when anhydrous combine with water when mixed with it. Their monohydrates may usually be obtained by precipitating a solution of one of their salts by the addition of a solution of one of the alkalis in slight excess. Hydrated cupric oxide has, however, the formula  $\text{CuO}, 2\text{H}_2\text{O}$ ; and the hydrated oxides of lead and tin consist of  $2\text{PbO}, \text{H}_2\text{O}$ , and  $2\text{SnO}, \text{H}_2\text{O}$ .

Most of the monoxides, by their reaction with the ordinary acids, form salts which are neutral in their action upon test-paper. The following equations may be taken as exemplifying some ordi-

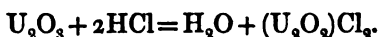
nary cases of the action of acids upon these oxides and their hydrates:—



3. *Sesquioxides*, of the type  $\text{N}'''\text{O}_3$ .—Most of the oxides of this class are feeble bases; among them are included alumina, and the sesquioxides of cerium, uranium, iron, manganese, chromium, antimony, and bismuth. They furnish salts when acted upon by acids, but all these salts redden litmus: usually 3 atoms of water are separated by the reaction of the base upon the acid; as, for instance,



These oxides of iron, antimony, and aluminum, however, occasionally, and uranic oxide invariably, form salts with the elimination of 1 atom of water only, two-thirds of the oxygen remaining in a state apparently of intimate combination with the metal; for instance:—



Sesquioxides of cobalt and nickel exhibit no tendency to form salts by reaction either with acids or bases. When heated with hydrochloric acid, they evolve chlorine and furnish a lower chloride; no chloride corresponding to these sesquioxides being known:—



Sesquioxide of arsenicum possesses no basic properties, but when dissolved in water is feebly but decidedly acid; the sesquioxide of gold is insoluble in water, but its hydrate ( $\text{H}_2\text{O}, \text{Au}_2\text{O}_3$ , or  $\text{AuHO}_2$ ) presents the properties of an acid, though they are but feebly marked.

The basic sesquioxides have but a feeble attraction for water; when precipitated by alkaline solutions from the solutions of their salts, they furnish very bulky gelatinous precipitates, which easily lose water during drying.

4. *Three-fourths Oxides*, of the type  $\text{N}_3\text{O}_4$  or  $\text{N}'''\text{O}, \text{N}'''\text{O}_3$ .—These oxides do not form salts with acids, being probably compounds of a protoxide with a sesquioxide, into the compounds corresponding to which they are resolved by the action of acids; as for instance:  $\text{Fe}_3\text{O}_4 + 8\text{HCl} = \text{FeCl}_2 + \text{Fe}_2\text{Cl}_6 + 4\text{H}_2\text{O}$ . Magnetic

oxide of iron,  $\text{Fe}_3\text{O}_4$  or  $\text{FeO}, \text{Fe}_2\text{O}_3$ , is the best representative of the class, which is rather numerous, and includes corresponding oxides of chromium, uranium, manganese, nickel, and cobalt, besides the double oxides, chrome ironstone,  $\text{FeO}, \text{Cr}_2\text{O}_3$ ; spinelle,  $\text{MgO}, \text{Al}_2\text{O}_3$ ; gahnite,  $\text{ZnO}, \text{Al}_2\text{O}_3$ .

5. *Dioxides* of the type  $\text{M}_2\text{O}_3$  or  $\text{N}^{\text{iv}}\text{O}_3$ .

Of these there are three distinct varieties.

The first variety comprises the basic oxides, of which the platinic oxide ( $\text{PtO}_2$ ) and palladic oxide ( $\text{PdO}_2$ ) are the most important; they are feeble bases, and with water form hydrates, such as ( $\text{PtO}_2, 2\text{H}_2\text{O}$ ).

The second variety is represented by the peroxides of sodium ( $\text{Na}_2\text{O}_2$ ) and silver ( $\text{Ag}_2\text{O}_2$ ), and those of barium ( $\text{BaO}_2$ ), manganese, and lead. These oxides do not form corresponding salts with acids, nor do they yield corresponding chlorides: they retain the second atom of oxygen but feebly. When heated with oil of vitriol they give off oxygen, and form a sulphate corresponding to the protoxide;  $2\text{MnO}_2 + 2\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + \text{O}_2 + 2\text{H}_2\text{O}$ . When treated with hydrochloric acid they either furnish hydric peroxide, or liberate chlorine and form water; as for example:—

1.  $\text{BaO}_2 + 2\text{HCl} = \text{BaCl}_2 + \text{H}_2\text{O}_2$ ;
2.  $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$ .

Of these dioxides some, as those of potassium and sodium, are decomposed with evolution of oxygen when thrown into water; baric dioxide forms the hydrate ( $\text{BaO}_2, 6\text{H}_2\text{O}$ ); whilst the peroxides of manganese, lead, and silver do not become hydrated, the three oxides last mentioned conduct the voltaic current: plumbic dioxide, indeed, exhibits some properties of a metallic anhydride, and when fused with the hydrated alkalies furnishes compounds known as plumbates, whilst water is evolved;  $2\text{KHO} + \text{PbO}_2 = \text{K}_2\text{PbO}_3 + \text{H}_2\text{O}$ .

In the third variety of dioxides the character of the metallic anhydrides is distinctly marked; such, for example, as the stannic and the titanous anhydrides, with which silica and zirconia ought also to be classed: these oxides do not unite with water when placed in contact with it, but yield hydrates possessed of feebly marked acid characters when precipitated with due precautions from their combinations. For each of these dioxides a corresponding chloride, containing 4 atoms of chlorine, may be obtained.

6. *Trioxides*, of the type  $\text{N}^{\text{vi}}\text{O}_3$ .

This class includes the metallic anhydrides in which the acid property is most strongly developed; such, for example, as chromic,

molybdic, tungstic, and ruthenic anhydrides. Although the ferric and manganic anhydrides have not been isolated, their place is obviously in this group. The molybdic, tungstic, and ruthenic anhydrides are insoluble in water.

7. *Anhydrides*, of the type  $R^v_2O_5$ .

Arsenic, vanadic, and antimonie anhydrides,  $As_2O_5$ ,  $V_2O_5$ , and  $Sb_2O_5$ , are the representatives of this group of oxides: when combined with water they furnish well-marked metallic acids. Arsenic anhydride is deliquescent and freely soluble; vanadic anhydride is slightly soluble; the antimonie compound does not combine with water when mixed with it.

The properties of the metallic acids or hydrated compounds obtained by the action of these dioxides, trioxides, and peroxides upon water, directly or indirectly, will be referred to again hereafter, when the bodies themselves are described.

The compounds of the same metal with oxygen are often numerous; and the extremes, or the oxide with the maximum of oxygen, and the oxide with the minimum of oxygen, frequently present chemical qualities of opposite kinds, the former being electronegative, and possessing acid properties, whilst the lower oxides are electropositive, or basic in their nature.

An excellent instance of this kind is afforded in the various oxides of manganese: the protoxide ( $MnO$ ) is a powerful base; the sesquioxide ( $Mn_2O_3$ ) is a much weaker base; the red oxide ( $MnO, Mn_2O_3$ ) is a saline or indifferent oxide, and shows little disposition to furnish corresponding salts by reaction either upon acids or alkalis, and the same may be said of the black oxide ( $MnO_2$ ); while the two higher oxides, which, however, are only known in combination either with hydrogen or the metals, are soluble in water, when they constitute the manganic and permanganic acids ( $H_2MnO_4$ , and  $HMnO_4$ ). As a general rule, the greater the number of atoms of oxygen which an oxide contains, the less is it disposed to form salts by reaction with the acids; on the contrary, its hydrate frequently possesses acid properties, and then it reacts upon bases to form salts.

The basic oxides in general are devoid of all metallic appearance, and present *par excellence* the characters of earthy matters. The protoxides, when solid, are all insulators of the voltaic current; but some of the higher oxides, such as the peroxides of silver, lead, and manganese, allow it to pass with facility. It is singular that all these conducting peroxides may be formed in solutions of salts of their respective metals by the action of the current itself.

The oxides, when found crystallized in the native state, are much harder than the metals that furnish them, and they generally have a specific gravity considerably less than that of the metals themselves. All the oxides are solid at ordinary temperatures; many of them are fusible at a red heat, such, for example, as the protoxides of potassium, sodium, and lead, and the sesquioxide of bismuth: but cupric oxide, molybdic trioxide, chromic sesquioxide, and black oxide of iron, require a much higher temperature to effect their fusion. Baryta, strontia, and alumina require the heat of the oxyhydrogen jet; while some oxides, such as lime and yttria, exhibit no appearance of fusion, even after the application of this intense heat.

As a general rule, the addition of oxygen to a metal renders it much less fusible and volatile. Ferrous oxide, chromic sesquioxide, and molybdic trioxide, are the only oxides which melt at a temperature below that of the metal from which they are produced. A few of the oxides are volatile at moderate temperatures; among these are arsenious and antimonious sesquioxide and osmic tetroxide. Nine only of the basic oxides are soluble in water to any considerable extent—viz., the five alkalis, and baryta, strontia, lime, and thallous oxide. The insolubility of the oxides, however, is far from being so complete in general as that of the corresponding sulphides, and consequently, except in particular cases, it is less advisable in analytical operations to separate the metals in the form of oxides than in that of sulphides; the oxides of lead, silver, and mercury in particular, are perceptibly soluble in pure water.

Those hydrated compounds of oxygen with the metals which possess acid characters—such as the chromic, manganic, and arsenic acids—are often freely soluble in water; but even those acids, which, like the tantalic, molybdic, and tungstic, are nearly insoluble, usually reddened litmus-paper, though their anhydrides have no such effect.

*Preparation.*—Most of the oxides may be procured in combination with water; generally speaking, these hydrated oxides are obtained by double decomposition, on the addition of the solution of an alkali to one of their soluble salts: in this manner zincic sulphate yields hydrated zincic oxide on adding potassic hydrate to its solution;  $\text{ZnSO}_4 + 2\text{KHO} = \text{K}_2\text{SO}_4 + \text{ZnH}_2\text{O}_2$ . The metals which form powerful bases, like the alkalis and alkaline earths, retain the water with great obstinacy; while others, which are less powerful bases, such as hydrated cupric oxide, are decomposed at a temperature below that of boiling water.

The anhydrous oxides may be obtained in several ways:—

- 1.—They may often be formed directly, by burning the metal in air, or in oxygen gas. This process is best adapted to metals which, like zinc or arsenicum, are volatile, or which produce fusible oxides, like iron or lead; in such cases the oxide is removed as fast as it is formed, and fresh surfaces of the metal are continually exposed to the action of the gas. Anhydrous potash and soda are obtained by this method; and it is resorted to on the large scale in the preparation of arsenious anhydride, and of the oxides of zinc and lead. Several of the metallic protoxides, if roasted at a low red heat in a current of air or of oxygen, absorb an additional quantity of oxygen. Litharge, or protoxide of lead, is thus converted into red lead,  $2\text{PbO}, \text{PbO}_2$ ; and baric dioxide,  $\text{BaO}_2$ , may in this way be obtained from baryta.
- 2.—Another method consists in the formation of a nitrate of the metal by means of nitric acid; the nitrate is then decomposed by heat, which expels the elements of the anhydride and leaves the oxide: in this way the oxides of mercury, bismuth, antimony, copper, barium, and strontium are prepared.
- 3.—In some cases it is found advantageous to prepare the oxide by the decomposition of the carbonate of the metal by heat. All the carbonates, with the exception of those of cæsium, rubidium, sodium, potassium, and barium, are decomposed at a red heat; lithic carbonate, however, is only incompletely decomposed. Lime is thus commonly obtained from limestone, which is an impure carbonate.
- 4.—Sometimes the hydrated oxide is first precipitated, as already mentioned, and then rendered anhydrous by heat; in this manner the ferric and uranic oxides are often prepared.
- 5.—Occasionally the ignition of a sulphate is resorted to, as in preparing alumina and ferric oxide.
- 6.—All the acid oxides may be obtained by deflagrating the metal or its sulphide with nitre; the tendency of the metallic acid to form a salt by reaction with the alkali favours the oxidation of the metal: the higher oxides of osmium, titanium, manganese, and chromium, as well as of some other metals, may be obtained in this way.

*Decompositions.*—1. By the action of a *red heat* many of the oxides lose their oxygen, either partially or entirely. The oxides of gold, silver, mercury, platinum, and palladium may thus be completely reduced; the peroxides of lead, cobalt, nickel, and barium, return to the state of protoxide; and the metallic anhydrides lose a portion of their oxygen; for example, arsenic and chromic anhydrides are thus converted respectively into arsenious anhydride and chromic oxide. The higher oxides of

iron and manganese furnish the magnetic oxide,  $\text{Fe}_3\text{O}_4$ , and the red oxide  $\text{Mn}_2\text{O}_4$ . It may be stated as a general rule, liable however to exception, especially in the case of the acidifiable metals, that the attraction of a metal for oxygen increases in the inverse proportion of its specific gravity; the lightest metals, such as potassium and sodium, being the most readily oxidized, while platinum, iridium, and gold, which are the densest metals, are also those which show the smallest tendency to combine with oxygen.

2.—The oxides are not affected by *hydrogen* gas at the ordinary temperature of the air. All the higher oxides of the metals are readily reduced to protoxides by hydrogen at a low red heat, whilst water is formed; and at a full red heat a large number of them are reduced to the metallic state. This reduction goes on most readily when the current of hydrogen is brisk, so that the vapour of water is carried away as fast as it is formed. The oxides of many of the metals which decompose water at a red heat may nevertheless be deprived of their oxygen in a brisk current of hydrogen; this is the case, for example, with the oxides of iron, zinc, and cadmium; but not with those of chromium or manganese. The alkalis and the earths are not reducible by hydrogen.

3.—The reducing action of *carbon* at a high temperature is still more important; all the metals which yield their oxygen to hydrogen do so to carbon, and potassium and sodium are obtainable from their compounds by its agency. This arises in part from the volatility of these two metals, which is sufficient to enable them to be distilled from the carbonaceous mixture. Lithium and the metals of the earths are not sufficiently volatile to pass over in vapour, and though their attraction for oxygen is less intense than that of potassium or of sodium, they cannot be obtained from their oxides by the action of carbon. It depends upon the nature of the metal, and upon the temperature employed, whether the gas that is formed during the reduction be carbonic oxide or carbonic anhydride. The more readily oxidizable metals, such as potassium, zinc, and iron, at a high temperature decompose carbonic anhydride, so that carbonic oxide only is formed when they are reduced; while if the reduction takes place readily, as is the case with copper and lead, carbonic anhydride is obtained.

4.—Dry *chlorine* sometimes even without the application of heat, decomposes the basic metallic oxides, such as argentic and mercuric oxide, expelling their oxygen, and converting them into

chlorides. At an elevated temperature few of them, excepting magnesia and the earths in the third group, resist its action: the oxides of gold and platinum are simply reduced to the metallic state, but chlorides of the metals are formed in other cases.

If the oxides be hydrated and suspended in water, the action of chlorine is quite different; the metals of the first two groups yield bleaching compounds, and by heat are converted into chlorates and chlorides, in the manner already explained (379). The oxides of the third group, the earths proper, experience no particular change, but those in the ferric group are converted into a mixture of chloride and hydrated sesquioxide. The sesquioxides of cobalt and nickel are usually prepared in this manner: for example,  $3\text{CoH}_2\text{O}_3 + \text{Cl}_2 = \text{CoCl}_2 + \text{Co}_2\text{O}_3, 3\text{H}_2\text{O}$ .

If the liquid be strongly alkaline, the whole of the metal may be converted into sesquioxide;  $2\text{CoH}_2\text{O}_3 + 2\text{KHO} + \text{Cl}_2 = \text{Co}_2\text{O}_3, 3\text{H}_2\text{O} + 2\text{KCl}$ . The potash in this case parts with its oxygen, which is transferred to the cobalt, whilst the chlorine combines with the potassium. The protoxide of manganese, under these circumstances, yields the hydrated peroxide,  $\text{MnO}_2, 2\text{H}_2\text{O}$ .

If the metal be capable of forming an acid with 3 atoms of oxygen, the process of oxidation may even proceed further, and the sesquioxide may, in the presence of a large quantity of potash, become converted into the metallic acid, which reacts upon a portion of the excess of alkali and forms a salt, as in the case of ferric oxide, when potassic ferrate is produced;  $\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O} + 10\text{KHO} + 3\text{Cl}_2 = 2\text{K}_2\text{FeO}_4 + 6\text{KCl} + 8\text{H}_2\text{O}$ .

5.—Most of the oxides are decomposed more or less completely when heated with *sulphur*; the alkalis and alkaline earths are converted into a mixture of sulphate and sulphide, but magnesia, chromic oxide, stannic, and titanic anhydrides, as well as the metals of the earths proper, are unaltered. Most of the other oxides are converted into sulphides, with escape of sulphurous anhydride. The oxides are more readily decomposed by sulphur if they be previously mixed with carbon.

(534) *Estimation of Oxygen in Metallic Oxides*.—The composition of a metallic oxide may be ascertained, if it be decomposable by hydrogen, by heating the compound in a current of this gas, collecting and weighing the water produced, and determining the amount of reduced metal which a given weight of the oxide has yielded. In other cases the composition of the oxide is determined synthetically, a given weight of the metal being converted into oxide, either by heating the metal in a current



of air, or by converting it into a nitrate, and afterwards expelling the elements of nitric anhydride by the application of heat, and weighing the quantity of oxide which is left.

(535) **SULPHIDES.**—The combinations of sulphur with the metals are numerous; they are in many instances of great value, and form important ores. A large number of the native sulphides often exhibit a high metallic lustre, as is shown by the sulphides of iron, copper, lead, and antimony.

Sulphur frequently combines with the same metal in several proportions, and it usually happens that for each oxide a corresponding sulphide may be formed; the sulphides, indeed, present a close analogy with the oxides. Sometimes, as in the case of the metals of the alkalis and alkaline earths, the sulphides are more numerous than the oxides: for instance, three oxides of potassium and sodium, and two only of barium are known, but there are not fewer than five sulphides of each of these metals.

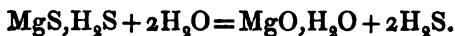
All the metallic sulphides are solid at ordinary temperatures. Most of them may be fused at a heat a little above redness, and if the air be excluded, the protosulphides undergo no change in composition; but many of the higher sulphides, such as the ferric sulphide and stannic sulphide ( $\text{SnS}_3$ ), are decomposed, and give off the second atom of sulphur, whilst a lower sulphide of the metal is left. Arsenious sulphide, or orpiment ( $\text{As}_2\text{S}_3$ ), and mercuric sulphide, or cinnabar ( $\text{HgS}$ ), may be sublimed if excluded from the air; that is to say, they may be converted into vapour, and recondensed in the solid form; indeed, these sulphides are usually purified by this operation.

The sulphides of all the metals are insoluble in water with the exception of those of the alkali-metals and of strontium and barium. Calcic and magnesian sulphides, however, are sparingly soluble.

If solutions of the sulphides of the metals of the alkalis and alkaline earths be subjected to a current of gaseous sulphuretted hydrogen, they combine with it, and form soluble compounds which correspond to the hydrates of the oxides; for example—



The compounds thus formed have been termed *sulph-hydrates*, or *hydro-sulphides*. Those of calcium and magnesium are decomposed into hydrates by boiling with water; for example;—



Several of the hydrosulphides may be obtained in crystals, if evaporated in vessels from which air is excluded.

The sulphides, like the oxides, may be subdivided into basic and acid sulphides, according to the nature of the metal and the number of atoms of sulphur with which each atom of metal is combined. These may be supposed to be formed on the type of one or more atoms of sulphuretted hydrogen, as the oxides are upon the type of one or more atoms of water. The proto-sulphides of the alkali-metals afford illustrations of basic sulphides, and they enter into combination with the higher sulphides of metals which, like antimony and arsenicum, form acids with oxygen. Arsenic sulphide ( $\text{As}_2\text{S}_3$ ), in this way combines with disodic sulphide, and forms a crystalline soluble compound ( $3\text{Na}_2\text{S}, \text{As}_2\text{S}_3, 15\text{H}_2\text{O}$ ); and in like manner antimonious sulphide ( $\text{Sb}_2\text{S}_3$ ), forms a soluble compound with disodic sulphide ( $3\text{Na}_2\text{S}, \text{Sb}_2\text{S}_3, 18\text{H}_2\text{O}$ , or  $\text{Na}_3\text{SbS}_4, 9\text{H}_2\text{O}$ ), which crystallizes in beautiful transparent tetrahedra. A large number of similar compounds may be formed with the sulphides of other metals, and these compounds are for the most part soluble in water.

In consequence of the tendency to the formation of these double sulphur salts, many of the sulphides which are insoluble in water are dissolved freely by solutions of sulphide of potassium or of sulphide of ammonium; and this circumstance is frequently taken advantage of in the laboratory during the progress of an analysis, for the purpose of separating certain metals, the sulphides of which are soluble in solutions of the sulphides of the alkali-metals, from others which are not soluble in these compounds. The following sulphides may be dissolved by a solution of ammoniac sulphide, and by a solution of dipotassic sulphide:—

Auric sulphide ...	$\text{Au}_2\text{S}_3$	Vanadic persulphide ...	$\text{V}_2\text{S}_5$
Platinic sulphide ...	$\text{PtS}_2$	Tungstic trisulphide ...	$\text{WS}_3$
Rhodic sulphide ...	$\text{Ro}_2\text{S}_3$	Molybdic trisulphide ...	$\text{MoS}_3$
Arsenious sulphide ...	$\text{As}_2\text{S}_3$	Molybdic tetrasulphide ...	$\text{MoS}_4$
Arsenic sulphide ...	$\text{As}_2\text{S}_5$	Stannous sulphide ...	$\text{SnS}$
Antimonious sulphide ...	$\text{Sb}_2\text{S}_3$	Stannic sulphide ...	$\text{SnS}_2$
Antimonic sulphide ...	$\text{Sb}_2\text{S}_5$	The sulphides of tellurium.	
Vanadic tetrasulphide ...	$\text{V}_2\text{S}_4$	The sulphides of iridium.	

The double salts thus obtained are decomposed by the addition of an acid, such as the sulphuric or the hydrochloric, sulphuretted hydrogen being evolved, whilst the sulphide of the electronegative metal is precipitated; for example,  $3\text{Na}_2\text{S}, \text{Sb}_2\text{S}_3 + 6\text{HCl}$  become  $6\text{NaCl} + \text{Sb}_2\text{S}_3 + 3\text{H}_2\text{S}$ .

These electronegative sulphides are often soluble in solutions

of the alkalis, forming a mixture of a sulpho-salt with an oxy-salt. Antimonious sulphide, for instance, when dissolved in caustic potash, gives the following result ;  $\text{Sb}_2\text{S}_3 + 6\text{KHO} = \text{K}_3\text{SbO}_3 + \text{K}_3\text{SbS}_3 + 3\text{H}_2\text{O}$ .

*Decompositions.*—If free oxygen or atmospheric air be allowed access to the heated sulphides, they are all decomposed ; the sulphur becomes oxidized, and passes off as sulphurous anhydride ( $\text{SO}_2$ ), whilst the metal, in most cases, as occurs with tin, antimony, and molybdenum, remains in combination with oxygen. The sulphides of the metals of the alkalis and of the alkaline earths become converted into sulphates of the metal, and the same thing occurs less completely with many of the metals which have a strong attraction for oxygen ; the sulphides of iron, lead, and copper, are partially converted into sulphates, but by a stronger heat these sulphates afterwards lose their acid, and the oxide of the metal only is left. The sulphides of the noble metals, when roasted in a current of air, lose their sulphur, which burns off in the form of sulphurous anhydride, while the pure metal remains behind, though in the case of silver a portion of argentic sulphate is commonly formed.

Many of the hydrated sulphides become oxidized by exposure to the air, and generally they are converted into sulphates. The hydrated sulphides of iron, however, furnish hydrated sesquioxide of the metal, while sulphur is liberated : and the sulphides of the metals of the alkalis and alkaline earths become converted into hyposulphites ; for instance,  $2\text{CaS} + \text{H}_2\text{O} + \text{CO}_2 + 2\text{O}_2 = \text{CaS}_2\text{H}_2\text{O}_4 + \text{CaCO}_3$ .

A large number of the sulphides, especially those of the more oxidizable metals, such as those of iron, zinc, and manganese, are dissolved by diluted hydrochloric acid when cold, and still more readily when heated,—a chloride of the metal and hydrosulphuric acid being formed. Others, such as those of nickel, cobalt, and lead, require boiling with the concentrated acid : it is in this way that hydrochloric acid acts upon antimonious sulphide :  $\text{Sb}_2\text{S}_3 + 6\text{HCl}$  becoming  $2\text{SbCl}_3 + 3\text{H}_2\text{S}$ . Sulphuric acid, when diluted, acts in a similar manner upon the sulphides of the more oxidizable metals, though less readily than hydrochloric acid.

The sulphides are all decomposed when heated in a current of chlorine gas, chloride of sulphur and chloride of the metal being formed. This property is sometimes made use of in the analysis of ores consisting chiefly of sulphides, or of sulphides and arsenides of the metals ; the volatile metallic chlorides are in this way separated from the more fixed ones. Aqua regia attacks and de-

composes the sulphides as readily as gaseous chlorine; and a mixture of hydrochloric acid and potassic chlorate is equally effectual in decomposing them. With the exception of mercuric sulphide, they are also decomposed by nitric acid, sulphuric acid and nitrate of the metal being formed; during this operation part of the sulphur is often separated in the form of tough elastic masses, which, if the heat be continued, collect into yellow globules, and can be oxidized only by prolonged digestion in the acid.

When the sulphides are fused with the alkaline carbonates or with the hydrated alkalis, they are partially decomposed, and the mass contains a variable mixture of sulphide with oxide of the alkali-metal, and different oxy-salts of sulphur.

Before the blowpipe the sulphides are easily recognized by the odour of sulphurous anhydride which they emit, either when heated in a glass tube open at both ends, or when roasted upon charcoal. Some other particulars relating to the sulphides have been already mentioned (428).

*Preparation.*—Many methods for preparing the sulphides may be adopted. 1.—Sulphur may be heated with the metallic oxides, many of which it decomposes: with the alkalis and alkaline earths, a sulphate, and a sulphide with variable proportions of sulphur, are obtained; but when definite and pure sulphides are required, other means should be adopted. 2.—The lowest sulphides of the metals of the alkalis and alkaline earths may be procured by decomposing their sulphates by igniting them in closed vessels with charcoal; oxygen is removed, carbonic oxide formed, and the remaining sulphide may be dissolved in water and freed from the excess of charcoal;  $K_2SO_4 + 4C = K_2S + 4CO$ . 3.—Hydrogen is sometimes employed for preparing the sulphides from the sulphates, which are to be placed in a tube and ignited in a current of the gas. In this manner the protosulphides of the alkali-metals are easily obtained, but the sulphates of the other metals frequently lose a portion of the sulphur, as well as all their oxygen, and subsulphides are procured. 4.—Many of the metals combine directly with sulphur, if heated with it, and form sulphides; but the compounds thus obtained often contain sulphur dissolved in, or disseminated through, the mass. Ferrous sulphide is usually prepared in this manner. Vermilion, and realgar are also often prepared by the direct union of their constituents. Indeed, sulphur, though itself combustible, supports the combustion of many metallic bodies, which burn vividly when heated in its vapour. 5.—In other cases the sulphides may be formed by heating the metal in a current of sulphuretted hydrogen,

or in the vapour of carbonic disulphide. This latter method is the plan commonly adopted in procuring titanous sulphide from titanous anhydride;  $\text{TiO}_2 + \text{CS}_2 = \text{TiS}_2 + \text{CO}_2$ . 6.—Hydrated sulphides of the metals of the last three groups may also be procured by passing a stream of sulphuretted hydrogen through neutral or acid solutions of their salts, when they are precipitated in the insoluble form. 7.—The hydrated sulphides of zinc, iron, manganese, cobalt, and nickel are not thrown down by sulphuretted hydrogen in acidulated solutions, but may be prepared by double decomposition, by mixing a neutral solution of the salts of any of these metals with that of a sulphide of one of the alkali-metals: thus manganous sulphate if mixed with dipotassic sulphide yields potassic sulphate and manganous sulphide.  $\text{MnSO}_4 + x\text{H}_2\text{O}, \text{K}_2\text{S} = \text{K}_2\text{SO}_4 + x\text{H}_2\text{O}, \text{MnS}$ . In many cases the colours of these hydrated sulphides are characteristic of the metal:—for example, the hydrated sulphide of zinc is white; that of manganese flesh-red; those of cadmium and arsenicum are yellow, as is also stannous sulphide; and hydrated stannous sulphide is chocolate-brown. The sulphides of molybdenum, rhodium, iridium, and osmium are brown, each with its peculiar shade; whilst in a large number of instances—including the sulphides of iron, cobalt, nickel, uranium, vanadium, bismuth, copper, lead, silver, mercury, gold, platinum, and palladium—the precipitated sulphides are of a black, more or less pure.

(536) *Estimation of Sulphur in Metallic Sulphides.*—Sulphur is always estimated in the form either of a sulphate or of free sulphur. The sulphur in a sulphide is easily converted into a sulphate by the agency either of gaseous chlorine or of aqua regia; and the soluble sulphates, when mixed in slightly acid solution with a salt of barium, yield the insoluble baric sulphate, the amount of which, after it has been well washed with boiling water and ignited, furnishes data for the calculation of the sulphur; 100 parts of baric sulphate representing 34·34 of sulphuric anhydride, or 13·74 of sulphur. If a salt of silver be present, baric nitrate must be employed to precipitate the sulphuric acid.

If during the solution of a sulphide in aqua regia, the sulphur have collected into clear yellow balls, and the action upon the ore appears to be complete, it is not necessary to wait till the whole of the sulphur is dissolved: the undissolved portion may be collected on a small counterpoised filter, and weighed, and its amount must be added to that which has been converted into sulphuric acid, the proportion of which is to be ascertained by means of a barium salt in the manner above described.

(537) THE SELENIDES and TELLURIDES are closely analogous to the sulphides in general characters, but they are too rare to need particular description. The presence of selenium in a compound is readily ascertained by the peculiar odour which it emits when heated in the reducing flame of the blowpipe.

(538) CHLORIDES.—Just as the different classes of oxides may be conceived to be formed from one or more atoms of water in which the hydrogen is displaced by metal, so the different varieties of chlorides may be referred to one or more atoms of hydrochloric acid, in which the place of the hydrogen is supplied by a metal.

The principal groups of chlorides are the following :—

1st. *Subchlorides*, „ $M_2Cl$  or  $NCl$ , on the type of  $HCl$  ; as

Argentous chloride . . . . .  $Ag_2Cl$ .

Calomel (Mercurous chloride) . . .  $HgCl$ .

2nd. *Monochlorides*,  $M'Cl$ , formed on the type of  $HCl$  ; as

Potassic chloride . . . . .  $KCl$ .

3rd. *Dichlorides*,  $N''Cl_2$ , on the type of  $H_2Cl_2$  ; such as

Calcic chloride . . . . .  $CaCl_2$ .

4th. *Trichlorides*,  $N'''Cl_3$ , on the type of  $H_3Cl_3$  ; such as

Antimonious chloride . . . . .  $SbCl_3$ .

5th. *Hexachlorides*,  $R^vCl_6$ , or  $N''''Cl_6$ , on the type  $6HCl$  ;  
such as

Molybdic chloride . . . . .  $MoCl_6$

Aluminic chloride . . . . .  $Al_3Cl_6$ .

6th. *Tetrachlorides*,  $R^ivCl_4$ , on the type of  $H_4Cl_4$  ; such as

Platinic chloride . . . . .  $PtCl_4$ .

7th. *Pentachlorides*,  $R^vCl_5$ , on the type of  $H_5Cl_5$  ; such as

Antimonic chloride . . . . .  $SbCl_5$ .

1. The basic chlorides, or *subchlorides*, are few in number and of small importance ; they are insoluble in water, argentous chloride, cupreous chloride, and calomel, comprising all that are of interest.

2. The *Monochlorides*, or *Protochlorides*, form an important group, including the chlorides of the alkali-metals, and those of silver and thallium, as well as aurous chloride. Aurous and argentic chlorides are insoluble in water ; thallous chloride is but sparingly soluble. Aurous chloride is decomposed by a heat below redness, but the other chlorides fuse readily when heated, and may even be slowly volatilized without decomposition. They are conductors of the voltaic current when fused.

3. *Dichlorides*.—The compounds contained in this group are

formed by the union of 1 atom of a metallic dyad with 2 atoms of chlorine. They present characters which are similar to those of the foregoing group, to which, indeed, they bear the closest resemblance: they were till quite recently considered to form part of it, these chlorides having been, in fact, usually described as protochlorides.

Amongst the members of this group are the chlorides of many highly basylous metals, such as barium and calcium. The chlorides of the electronegative dyads, like that of mercury, are strongly opposed to these basylous chlorides in properties. All the chlorides of this group, when anhydrous, are solid at common temperatures; but when heated in vessels from which air is excluded, they may all be melted without undergoing decomposition, except those of copper, platinum, and palladium. Cupric chloride loses half its chlorine and becomes converted into cupreous chloride, whilst platinous chloride,  $\text{PtCl}_2$ , and palladious chloride are decomposed into free chlorine, and a residue of the pure metal. Several of the chlorides remain semi-transparent after fusion, and furnish soft and sectile masses, somewhat horny in aspect. Many of these chlorides, such as those of zinc and mercury, may be distilled without decomposition. Plumbic chloride is but sparingly soluble; platinous chloride, in one of its modifications, is quite insoluble; the other members of the group are freely soluble in water.

4. The next group comprises those known as *trichlorides* or *terchlorides*, of which the following are the most important:—

Arsenious chloride	...	...	...	...	$\text{AsCl}_3$
Antimonious chloride	...	...	...	...	$\text{SbCl}_3$
Bismuth trichloride	...	...	...	...	$\text{BiCl}_3$
Auric chloride	...	...	...	...	$\text{AuCl}_3$

Auric chloride is decomposed into aurous chloride by a moderate heat, and at a higher temperature loses all its chlorine; the other three chlorides may be volatilized unchanged by a moderate elevation of temperature. They are decomposed by the addition of water; arsenious chloride into arsenious acid and hydrochloric acid,  $\text{AsCl}_3 + 3\text{H}_2\text{O} = 3\text{HCl} + \text{H}_3\text{AsO}_3$ ; whilst the chlorides of antimony and bismuth furnish oxychlorides;  $3\text{SbCl}_3 + 3\text{H}_2\text{O} = \text{SbCl}_3, \text{Sb}_2\text{O}_3 + 6\text{HCl}$ .

5. Parallel in properties with these volatile trichlorides are the *hexachlorides* of two other acidifiable metals:—

Perchloride of molybdenum	...	...	...	...	$\text{MoCl}_6$
„ tungsten	...	...	...	...	$\text{WCl}_6$

These chlorides are volatile, and are decomposed by water.

The substances, formerly called *Sesquichlorides*, constitute a

remarkable group, of which the most important are aluminic chloride, ferric chloride, and chromic chloride. Each of these compounds contains 1 atom of the metallic element united with 3 atoms of chlorine, but each may be volatilized at a high temperature without decomposition; the vapour density of the chlorides of aluminum and iron has been ascertained by experiment, and the result is remarkable, since if  $HH=2$  vols.,  $Al_2Cl_6$  is also  $=2$  vols.: hence their formulæ should be doubled, as follows:—

Aluminic chloride	...	...	...	$Al_2Cl_6$
Ferric chloride	...	...	...	$Fe_2Cl_6$
Chromic chloride (judging by analogy)	...	...	...	$Cr_2Cl_6$

The aqueous solutions of these chlorides undergo partial decomposition when evaporated, hydrochloric acid escapes, and a considerable portion of oxide of the metal is formed.

6. Next we have a group of chlorides formerly described by chemists as the bichlorides, but now considered as *tetrachlorides*—viz.,

Silicic chloride	...	$SiCl_4$	Tungstous chloride	...	$WCl_6$
Titanic chloride	...	$TiCl_4$	Platinic chloride	...	$PtCl_6$
Stannic chloride	...	$SnCl_4$	Palladic chloride	...	$PdCl_6$
Zirconic chloride	...	$ZrCl_4$	Iridic chloride	...	$IrCl_6$
Molybdous chloride	...	$MoCl_5$	Ruthenic chloride	...	$RuCl_6$

The first three compounds are liquid at ordinary temperatures: they are densely fuming when exposed to the air; they may be distilled unaltered. With the exception of the tetrachlorides of platinum, palladium, iridium, and ruthenium, which by a high temperature are decomposed into metal and free chlorine, the remaining compounds are fusible volatile solids, and may be sublimed unaltered in vessels from which air is excluded. The tetrachlorides of tin, titanium, and the noble metals, form crystallizable double salts with the chlorides of the alkali-metals.

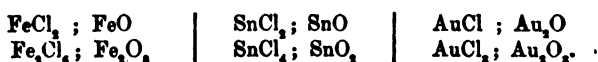
7. The *Pentachlorides* are represented by pentachloride of antimony, which corresponds with pentachloride of phosphorus. It is fuming and volatile, is decomposed by water, forming an oxychloride if the proportion of water is small, but yielding hydrated metantimonic acid, with separation of all its chlorine as hydrochloric acid, if the quantity of water be large.

At ordinary temperatures the action of chlorine upon the metals is generally stronger than that of oxygen upon them; but if a metallic chloride be heated in a current of oxygen or of atmospheric air, the chlorine is expelled, and an oxide of the metal is produced. The only instances in which this decomposition does not take place, occur in the case of the

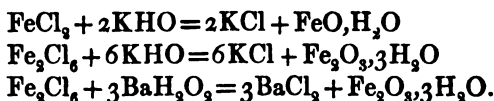


chlorides of the noble metals and in those belonging to the first and second groups.

In the case of the metals which have but slight attraction for oxygen, the chlorides generally correspond in number with the oxides; and for every chloride an analogous oxide is always obtainable, one atom of oxygen occupying the position of two atoms of chlorine in the compound. For instance, the corresponding chlorides and oxides of iron, tin, and gold are the following:—



Yet it is easy to obtain the oxides from solutions of the chlorides by precipitation; for example, in the case of the compounds of iron, the following reactions may be observed:—



When the metal exhibits a strong attraction for oxygen, and forms a powerful base, the number of oxides frequently exceeds that of the chlorides.

In many cases chlorine unites with the oxides of the metals. If the oxide of the metal be soluble in water, the *oxychloride* which is formed is soluble likewise, and the compound is remarkable for its bleaching properties. Chloride of lime ( $\text{CaOCl}_2$ ), and chloride of potash ( $\text{K}_2\text{OCl}_2$ ), furnish instances of this kind. Sometimes the chloride of a metal combines with its oxide and forms an insoluble oxychloride, as is the case with the oxychloride of mercury ( $3\text{HgO}, \text{HgCl}_2$ ). It is a still more frequent occurrence that a chloride of one of the alkali-metals combines with a chloride of one of those metals which have a feeblor attraction for oxygen, and the oxides of which partake rather of the character of acids than of bases. Thus we have a double chloride of platinum and potassium ( $2\text{KCl}, \text{PtCl}_4$ ) and a double chloride of gold and sodium ( $\text{NaCl}, \text{AuCl}_3, 2\text{H}_2\text{O}$ ). Indeed, the higher chlorides of the noble metals generally form double salts of this nature; and the same thing holds true in very many cases with the corresponding bromides and iodides.

*Preparation.*—1. Many of the metallic chlorides may be formed by heating the metal in a current of dry chlorine: in this way the perchlorides of antimony and iron are procured. 2.—If the basic oxides be heated to redness in a current of dry chlorine, oxygen is expelled and a chloride of the metal remains; but this process is never adopted for procuring the chlorides. 3.—The sulphides are

generally more readily decomposed by a current of gaseous chlorine than the oxides: owing to the strong attraction of chlorine for sulphur, both the sulphur and the metal combine with the gas, chloride of sulphur, and a metallic chloride being produced. This process, however, is seldom employed except in the course of an analysis. 4.—In cases where the chloride is volatile, like that of aluminum, of glucinum, and of titanium, the oxide of the metal may be mixed with charcoal, and a current of dry chlorine transmitted over the mixture; the charcoal removes the oxygen in the form of carbonic oxide, and the chlorine, uniting with the metal, forms a chloride which volatilizes and becomes condensed in the cool part of the apparatus. 5.—In many cases the chloride may be obtained by transmitting dry hydrochloric acid gas over the oxide or the sulphide of the metal heated to low redness, the attraction of hydrogen for oxygen and for sulphur greatly facilitating the progress of the decomposition. 6.—An easier method, in cases where it is applicable, particularly when the hydrated chlorides are required, consists in dissolving the metal itself, its oxide, or its carbonate, in hydrochloric acid, and evaporating the solution till crystallization commences. Chloride of cobalt, of nickel, and of calcium may be thus obtained. This process, however, fails in many cases, if it be attempted to render the chloride anhydrous, particularly in the class to which the earths belong; chlorides of magnesium and aluminum, for example, lose their chlorine as hydrochloric acid when their solutions are evaporated;  $\text{MgCl}_2 + \text{H}_2\text{O} = \text{MgO} + 2\text{HCl}$ . 7.—In some cases chlorides of the metals, such as those of gold and platinum, are obtained by dissolving the metal in aqua regia, and decomposing any excess of nitric acid by evaporation to dryness with an excess of hydrochloric acid; a pure chloride of the metal may be obtained on re-dissolving the residue in water. 8.—Many of the chlorides of the more electronegative metals are decomposed when heated with the more basylous metals. Stannic chloride ( $\text{SnCl}_4$ ) may thus be obtained by heating metallic tin with an excess of corrosive sublimate; and trichlorides of antimony and bismuth may be obtained in a similar manner. Sometimes this process is employed for the purpose of isolating those metals the oxides of which resist decomposition by the usual means. In this way sodium is employed to decompose aluminic or magnesian chloride for the purpose of procuring the aluminum or magnesium in an uncombined form; and in a similar manner potassium is employed to obtain uranium from uranous chloride. 9.—The insoluble chlorides, such as argentic, plumbic, and mercurous chloride, may

be formed by the addition of hydrochloric acid, or of a soluble chloride, to a solution of the salts of these metals.

*Decompositions.*—All the metallic chlorides, excepting those of the metals of the alkalis and earths, are reduced when sufficiently heated in a brisk current of hydrogen. In many cases the reduction is easily effected, and this process is occasionally resorted to as a means of procuring certain metals in a state of purity. Iron, for example, may be obtained in fine cubic crystals by reducing ferrous chloride in this manner. It is necessary, however, to maintain a current of hydrogen of sufficient rapidity to carry away the hydrochloric acid from the reduced metal, as otherwise, in most cases, the chloride would be reproduced by the decomposition of the acid. All the chlorides, except those of the alkali-metals, and of barium and mercury, are decomposed when heated in a current of steam, generally leaving corresponding oxides, but chloride of bismuth leaves an oxychloride (Kunheim). All the soluble chlorides, when heated with sulphuric acid and black oxide of manganese, evolve chlorine gas. Other particulars relating to the chlorides have been already mentioned (373, 376).

(539) *Estimation of Chlorine in Metallic Chlorides.*—Chlorine is almost always estimated in the form of argentic chloride ( $\text{AgCl}$ ), 100 parts of which represent 24.74 of chlorine. The solution should be acidulated with nitric acid, and gently warmed, and then the argentic nitrate should be added. If iodine or bromine be present, it will be precipitated with the chlorine, and must be determined separately, and the corresponding weight of argentic iodide or bromide deducted.

The composition of an insoluble chloride or of a basic chloride may be ascertained, except in the case of argentic chloride, by boiling a given weight of the compound with a pure solution of potash, and then determining the quantity of chlorine in the alkaline solution by means of argentic nitrate: before adding the solution of silver, the alkaline liquid must be filtered from the undissolved metallic oxide, and acidulated with nitric acid.

(540) The BROMIDES (389, 391) closely resemble the chlorides in chemical characters, and may be arranged in corresponding groups: the bromides of the metals of the alkalis and alkaline earths may be prepared by digesting a solution of the alkali or of the earth with bromine in slight excess; a bromide and a bromate of the metal are thus formed, and by gentle ignition the bromate is decomposed, leaving a pure bromide: a small quantity of charcoal may be added previously to the ignition, by which the

decomposition of the bromate is more easily effected. The bromide is removed from the excess of charcoal by solution in water. The other bromides may be procured by acting upon the metals by bromine, either in a dry state or in the presence of water. They are also easily formed by dissolving the oxides or the carbonates in hydrobromic acid.

Bromine may be precipitated from its solutions, and, in the absence of chlorine, its quantity may be estimated, by means of argentic nitrate, which occasions a white precipitate of argentic bromide, 100 parts of which indicate 42.55 of bromine. If chlorine be present the precipitate will consist of a mixture of the bromide and chloride of silver: it must be collected and weighed, then digested with metallic zinc and a drop or two of sulphuric acid; in a day or two the zinc will have reduced the bromide and chloride to metallic silver; this must be well washed, dried, and weighed. It should be wholly soluble in nitric acid, since if it be not, a portion of the precipitate has escaped decomposition.

From the above data the relative proportions of the bromide and chloride of silver may be calculated:—let  $m$  be the weight of the mixed bromide and chloride, and let  $s$  be the weight of the reduced silver; then if  $x$  represent the proportion of bromide, and  $y$  that of chloride of silver, it will be found that

$$m = x + y, \quad \text{and } s = \frac{108}{143.5}x + \frac{108}{188}y;$$

consequently  $x$ , or the argentic bromide in the mixture,  $= m - y$ ; and  $y$ , or the argentic chloride in the mixture,  $= 5.6134 s - 3.2247 m$ .

(541) The IODIDES (396) may be formed by processes analogous to those employed for the bromides: the insoluble iodides, such as those of mercury, silver, and lead, may be obtained from a solution of potassic iodide, by mixing it with a solution of the metallic salt.

The iodides exhibit a strong tendency to form double salts, the iodides of the strongly basylous metals combining readily to form crystallizable double iodides with those of the electronegative metals, such as those of silver, mercury, and lead. The iodides also form double compounds with the oxides and chlorides: for example, there are several compounds of the iodide with the oxide of lead; and a combination of stannic chloride with the stannous iodide ( $\text{SnI}_2, \text{SnCl}_2$ ) may be obtained in orange-coloured crystals (Kane).

The quantity of iodine in a solution which contains iodides, if chlorides be absent, may be estimated by the addition of argentic nitrate slightly acidulated with nitric acid: the resulting buff-coloured argentic iodide, when collected and dried, contains 54.04 per cent. of iodine. If chlorine or bromine be present, the iodine must be precipitated by means of palladious nitrate; the precipitate must be allowed to subside during ten or twelve hours, and it may then be collected on a filter and dried at a temperature not exceeding  $158^{\circ}$  ( $70^{\circ}$  C.): this precipitate is insoluble in cold diluted nitric or hydrochloric acid, but soluble in ammonia. It contains 70.0 per cent. of iodine. Iodine may also be separated from bromine and chlorine, but less perfectly, by a mixture of ferrous sulphate and cupric sulphate (883).

(542) **FLUORIDES.**—The general properties of these compounds have been already stated (403). The fluorides are usually prepared by the direct action of hydrofluoric acid either upon the metal or more usually upon the oxide of the metal. Those which are insoluble may be procured by mixing a solution of the metallic salt with one of potassic or sodic fluoride.

*Estimation of Fluorine.*—A simple method of detecting and of approximatively estimating fluorine, when present, even in very small quantities, has been proposed by Dr. G. Wilson. The following is the process, slightly modified:—the substance, if it does not already contain silica, is mixed with pounded glass, placed in a retort, and made into a thin cream with oil of vitriol; the mixture is next heated, and distilled into a flask containing a solution of ammonia; the silicic fluoride comes over, and is immediately decomposed: on evaporating the liquid in the flask to dryness on a water-bath, the silica is rendered insoluble, and can be collected and weighed, whilst the ammoniac fluoride may be dissolved out with a little water, and the presence of fluorine shown by mixing it with oil of vitriol: the vapour which is evolved produces the usual corrosive action of hydrofluoric acid on glass (403): the proportion of silica in the insoluble residue to the fluorine, however, is not very uniform.

(543) **NITRIDES.**—It is not improbable that the fulminating compounds, obtained by digesting the hydrated oxides of gold, of silver, and of platinum, in a solution of ammonia, may owe their explosive character to the formation of a nitride: but the composition of these bodies has been only imperfectly investigated, on account of the ease with which they explode. So weak is the chemical attraction of nitrogen for most metallic bodies, that a slight alteration of circumstances often suffices to restore it sud-

denly to the gaseous state. Nitride of copper is formed by passing dry ammonia over cupric oxide, at a temperature not exceeding  $482^{\circ}$  ( $250^{\circ}$  C.), in which case water is formed at the expense of the hydrogen of the ammonia and the oxygen of the oxide, and part of the nitrogen escapes; thus,  $6\text{CuO} + 4\text{H}_3\text{N} = 2\text{Cu}_3\text{N} + 6\text{H}_2\text{O} + \text{N}_2$ . Nitrides of mercury and iron may be prepared by passing ammonia over mercuric and ferric oxide in a similar manner. Titanium, molybdenum, and vanadium absorb nitrogen rapidly at a red heat; and crystalline nitrides of chromium and magnesium have also been obtained.

(544) The PHOSPHIDES of the metals are of comparatively small importance: they are never met with in the native state. The phosphides of the metals of the alkalis and alkaline earths decompose water when thrown into it; self-lighting phosphuretted hydrogen is disengaged, and a hypophosphite of the metal is retained in solution. In some cases, as for example in that of calcic phosphide, the phosphide is formed by heating the oxide strongly, and driving the vapour of phosphorus over it; in this case it is mixed with a large proportion of calcic phosphate. The insoluble phosphides may often be obtained by transmitting a current of phosphuretted hydrogen through a solution of the salt of the metal in water; phosphides of copper and silver may be thus obtained.

When heated in air phosphides are converted into phosphates, or into phosphoric anhydride, while the metal is liberated.

(545) CARBIDES.—The only carbides of importance are those of iron, which will be considered in detail when treating of that metal. Manganese, palladium, iridium, and a few other metals, also combine with carbon; generally speaking, these carbides are more fusible than the metals which enter into their formation.

SILICON and BORON form with the metals analogous compounds of small importance. Amongst the most interesting of the silicides are those of calcium, aluminum, magnesium, iron, and copper.

(546) HYDRIDES.—Hydrogen is not known to combine with more than five metals:—viz., arsenicum, antimony, copper, iron, and potassium. The first two of these compounds are gaseous, and are decomposed by a red heat into metal and hydrogen gas. A solid hydride of arsenicum is also said to exist. A few metals, such as zinc and potassium, appear under peculiar circumstances to undergo partial volatilization along with the hydrogen at the moment that this gas is evolved.

## § III. HYPOTHESES ON THE CONSTITUTION OF SALTS.

(547) *Acids and Bases*.—It has already been stated (6) that any substance which is produced by the action of an acid upon a base is termed a salt. It is, however, necessary to examine more minutely into the nature both of bases and acids, and into that of the compounds formed by their combination with each other.

By the word *base*, is meant a body always of a compound nature, most frequently an oxide of a metal, which is capable of effecting a double decomposition with an acid, whilst a salt and water are formed, and the distinctive characters of the acid are more or less completely neutralized. A base, however, is not necessarily a metallic oxide; the hydrates of ammonia, quinia, and morphia, for example, are powerful bases, but they contain no metallic substance.

(548) *Oxyacids and Hydracids*.—When Lavoisier imposed upon one of the constituents of the atmosphere the name of oxygen, he supposed that the presence of that energetic body was essential to the existence of an acid; and this view was supported by the composition of the principal acids then known, such as the sulphuric, the sulphurous, the nitric, the carbonic, the phosphoric, and the boracic acids. The term acid was indifferently applied to the anhydrides and to the compounds produced by the action of anhydrides upon water; to which latter class of compounds the term is restricted by many later writers, and to which it is applied in this work. Lavoisier considered an acid to be an oxidized body more or less soluble in water, with a sour taste, capable of reddening vegetable blues, and entering into combination with the alkalies, the distinctive properties of which it neutralized.

By degrees, however, acids were discovered in which no oxygen could be detected: such, for example, as the hydrochloric, the hydriodic, and the hydrobromic, into the composition of which hydrogen enters; yet these bodies were found in other respects to correspond perfectly with Lavoisier's definition, and to possess all the characters of powerful acids. To meet this objection, the theory was modified, and the acids were divided into two great classes, the first of which comprised the *oxyacids*, such as the sulphuric, nitric, and others of analogous composition, in which it was supposed that the acid properties depended on the presence of oxygen; the second class was formed by the *hydracids*, such as the hydrochloric and hydriodic acids, in which hydrogen was an essential component. It was noticed, that when bodies belonging to either of these classes combine with metallic compounds, and

form neutral combinations, the acids do not unite directly with the metals without evolution of gas; with their *oxides*, on the contrary, combination appears to take place directly: diluted sulphuric acid, for example, has no action upon metallic copper, but it quickly dissolves its oxide, forming the blue solution of cupric sulphate. On applying heat so as to render the salt anhydrous, it was found that the salts of the oxyacids (of which sulphate of potash,  $KO,SO_3$ , may be taken as the type, adopting for the present the equivalents  $O=8$ ,  $S=16$ , and the old notation) might be represented under the form  $MO,SO_3$ , which supposes the union of 1 equivalent of the anhydride with 1 equivalent of a metallic oxide; while a hydracid (such, for instance, as hydrochloric acid) if made to act upon a base such as caustic soda, yields a body like common salt ( $NaCl$ ), which when dry contains neither hydrochloric acid nor soda, the radicle of the acid being left in combination with the metal itself:  $NaO,HO + HCl$  yielding  $NaCl + 2HO$ . Thus, in the case of the salts of the hydracids, it will be observed that the oxygen of the oxide is precisely sufficient to convert the hydrogen of the acid into water: this union, indeed, actually takes place, and the water so formed is expelled on the application of heat. When, therefore, a hydracid acts upon a base, a true double decomposition occurs.

In consequence of this supposed difference in constitution, it was proposed to subdivide salts into two classes,—the first, like nitrate of potash,  $KO,NO_3$ , being formed by the union of an oxide, such as potash, with an oxyacid, or anhydride as we now term it, such as the nitric; these were termed *oxysalts*: the other class being produced by the combination of a metal with the characteristic element in a hydrogen acid. The salts of the second class, being composed upon the same plan or type as sea-salt, were termed *haloid* salts (from  $\alpha\lambda\varsigma$ , sea-salt). This distinction is still recognized by many chemical writers. The supposition that a salt consists of an anhydride united to a base still affords the simplest explanation of many chemical decompositions; and it is scarcely possible to represent many of the complex silicates satisfactorily by any other plan.

(549) *Binary Hypothesis of Salts*.—The foregoing observations seem to prove that there is a marked difference between the composition of the oxyacid and the hydracid series of salts. The separation of salts into two classes, one consisting of the salts of the oxyacids, and the other of those of the hydracids, is not, however, indispensable. A hypothesis was advanced by Davy and by Dulong, which reduces all salts to the hydracid type. Upon



this view—frequently termed *the binary theory* of salts—all the hydrated acids are regarded as salts containing hydrogen in the place of a metal, so that hydrogen acts the part of a feeble basyl towards a group of elements, or a single element, which forms the radicle of the salt. It has already been shown that the anhydrides of those oxyacids which can be obtained in an isolated form, such, for example, as the sulphuric, the nitric, the phosphoric, the carbonic, and the boracic anhydrides, do not possess the properties generally admitted to constitute the true acid character. Sulphuric anhydride, for instance, does not redden dry litmus; it may be moulded in the fingers without injury; but when once it has passed into the hydrated form, which it speedily does by absorbing moisture from the air, it corrodes all organized substances with great activity. Carbonic anhydride is also without action on litmus. When such compounds have entered into combination with water they may be represented as hydracids, by a slight modification of the old formula; e.g., nitric acid ( $HO, NO_3$ ) may be expressed as  $(H, NO_3)$ , corresponding with hydrochloric acid ( $H, Cl$ ): each equivalent of these bodies, when heated in contact with a base or a metallic oxide, gives off 1 equivalent of water, in a manner precisely analogous to the hydracids already examined. One equivalent of oil of vitriol treated with 1 equivalent of oxide of lead would thus produce an equivalent of sulphate of lead and an equivalent of water;  $H_2SO_4 + PbO$  becoming  $Pb, SO_4 + HO$ .

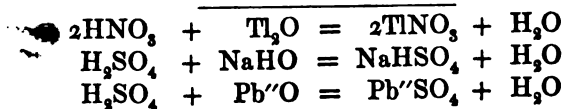
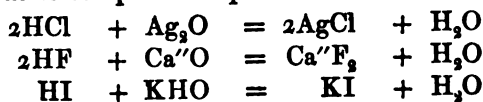
Most chemists indeed now regard the compounds which were previously considered as *hydrated acids* as salts composed of a compound radicle, which may be termed the *oxion* of the salt (consisting of the anhydride + an equivalent of oxygen) united with an equivalent of hydrogen. The other salts of the acid would be formed from these hydrogen compounds by the displacement of the hydrogen by an equivalent amount of each of the different metals which enter into the composition of the various salts, and which are indicated by their respective names. In accordance with this view, we have already given a simple explanation of the liberation of hydrogen when diluted sulphuric acid is acted upon by zinc; the zinc merely entering into combination with sulphion, and displacing the hydrogen; so that (resuming the notation which regards  $O=16$  and water  $H_2O$ )  $H_2SO_4 + Zn$  become  $ZnSO_4 + H_2$ ; and the reaction is, upon this view, analogous to that of the same metal upon hydrochloric acid;  $2HCl + Zn = ZnCl_2 + H_2$ .

A comparison of a few of the so-called hydracids with some of the hydrated oxyacids will show the similarity between them;

whilst the corresponding anhydrides will be at once seen to belong to an entirely distinct group of compounds :—

Hydracids.	Hydrated oxyacids.	Anhydrides.
HF	Nitric acid ... .. $\text{HNO}_3$	$\text{N}_2\text{O}_5$
HCl	Iodic " ... .. $\text{HIO}_3$	$\text{I}_2\text{O}_5$
HBr	Hypochlorous acid ... $\text{HClO}$	$\text{Cl}_2\text{O}$
HI	Sulphuric " ... .. $\text{H}_2\text{SO}_4$	$\text{SO}_3$

A few reactions between certain bases on the one hand with some of the hydracids, and on the other with certain hydrated oxyacids, will enable us to complete the parallel :—



In each case the salt is formed by the substitution of an equivalent amount of metal for hydrogen, whilst a corresponding quantity of water is liberated and occupies the place of the metallic oxide originally employed.

Binary compounds are such as consist of single atoms of two elements only; sodic chloride ( $\text{NaCl}$ ), therefore, is a binary compound; and if all salts be assimilated to this type, it is assumed that the grouping of their molecules resembles that which occurs in this binary compound. It has indeed been supposed that all salts consist of two portions: one comprising the distinctive constituents of the acid, and consisting either of a non-metallic elementary substance (chlorine,  $\text{Cl}$ , for example), which is termed the *radicle* of the salt, or else of an equivalent compound body (such as sulphion,  $\text{SO}_2$ ), which may be conveniently distinguished as the *oxion* in cases where the acid contains oxygen; the other is either a metal (sodium,  $\text{Na}$ , for instance), or else a compound like ammonium ( $\text{H}_4\text{N}$ ), equivalent to a metal, termed the *basyl* of the salt. It is easy to distinguish the oxions of acids in *ic* from those of acids in *ous*; by using in the latter case the termination *osion*;  $\text{SO}_2$ , the oxion of the sulphites being *sulphosion*,  $\text{NO}_2$ , the oxion of the nitrites, *nitrosion*, and so on. Attention has already been directed to the bearing of the electrolysis of saline compounds (286), upon this theory of their constitution.

(550) *Objections to the Binary Hypothesis.*—Notwithstanding the ingenuity of the foregoing hypothesis, and the advantages which

it offers in the explanation of certain modes of decomposition, it is open to many serious objections; and indeed it cannot be regarded as a correct representation of the composition of a salt under all circumstances. In fact, none of the compound radicles or oxions,  $\text{SO}_4$ ,  $\text{NO}_3$ ,  $\text{CO}_3$ , have been obtained in an isolated form, nor is it probable that they ever will be.

It also appears to be highly improbable that a body of such powerful chemical attractions as potash should, in potassic carbonate for example, part with its oxygen to a substance which, like carbonic anhydride, exhibits no tendency to further oxidation, so that  $\text{K}_2\text{O}, \text{CO}_2$  should become  $\text{K}_2\text{CO}_3$ .

The conclusion which is most probable is this: viz., that a salt, when once formed, must be regarded as a whole; it can no longer be looked upon as consisting of two distinct parts, but as a new substance, maintained in its existing condition by the mutual actions of all the elements which compose it. These different elements are not all united with each other in every direction with an equal amount of force. As in a crystal there are certain directions in which the mass admits of cleavage with greater facility than in others, and as two or three different directions of cleavage may be found in the same crystal by varying the direction in which the force is applied, so in the same salt there are directions in which it yields to the application of chemical force more readily than in others; and according as that chemical force is applied in one way or in another, the compound splits up into simpler substances, the nature of which will vary according to the mode which has been selected for effecting its decomposition.

For example, if the solution of a powerful acid, such as nitric acid, be poured upon potassic carbonate, carbonic anhydride is liberated abundantly, and potassic nitrate is produced;  $\text{K}_2\text{CO}_3 + 2\text{HNO}_3 = 2\text{KNO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ ; but if another portion of the same potassic carbonate be mixed with charcoal, and heated in an iron retort to whiteness, metallic potassium and carbonic oxide are the results;  $\text{K}_2\text{CO}_3 + 2\text{C} = \text{K}_2 + 3\text{CO}$ . Again, if a solution of potassic carbonate be subjected to electrolysis by the aid of the voltaic battery, the salt splits up into potassium (which is immediately oxidized by the water in the midst of which it is liberated), and into carbion,  $\text{CO}_3$ , which is as instantly resolved into oxygen gas and carbonic anhydride;  $2\text{K}_2\text{CO}_3$  becoming  $2\text{K}_2 + 2\text{CO}_3$ , and  $2\text{K}_2 + 4\text{H}_2\text{O}$  give  $4\text{KHO} + 2\text{H}_2$ , whilst  $2\text{CO}_3$  becomes  $2\text{CO}_2 + \text{O}_2$ . The probability therefore is, that neither the old nor the new view is absolutely correct, but that each may in turn well represent the salt when subjected to the influence of particular cir-

cumstances. It may therefore readily be conceded that the binary theory may in certain cases elucidate the decompositions observed, notwithstanding the difficulties which prevent its adoption as a correct representation of the molecular arrangement of saline compounds in general when in a quiescent state. On the other hand, it may often be convenient to represent certain salts as compounds of the anhydride and the base: calcic carbonate, for example, may sometimes be written  $\text{CaO}, \text{CO}_2$ , although the empirical formula  $\text{CaCO}_3$  may generally be preferred. So, again, in the case of the sulphates. Anhydrous magnesian sulphate may, for instance, be often written  $\text{MgO}, \text{SO}_3$ , although we may generally adopt the form  $\text{MgSO}_4$ , which involves no theory of its constitution.

(551) *Sulpho-Salts*.—The preceding remarks have been made with almost exclusive reference to those salts into the composition of which oxygen enters. There is, however, a numerous series of compounds parallel to these oxy-compounds, but in which sulphur enters into combination with the metal; and for each atom of oxygen in the series of the oxy-salts an equivalent of sulphur is substituted in the corresponding compound in the sulphur series. Generally speaking, the sulphur-salts are of subordinate importance to the oxy-compounds; many of them are decomposed by admixture with water, and they have been the subject of much less study and research than the oxy-salts. Many chemists regard these compounds as salts in which the electropositive sulphides, such as the protosulphides of potassium, &c., act the part of bases; and the electronegative sulphides, such as the higher sulphides of arsenic and antimony, act as acids. No doubt their molecular constitution is analogous to that of the oxy-salts.

(552) *Varieties of Salts*.—Salts are usually spoken of as *neutral*, *acid*, or *basic*; but though these terms are in general use, there is some ambiguity in the manner in which they are applied.

(553) *Neutral, or Normal Salts*.—The idea of neutrality implies that the peculiar characters both of the acid and of the alkali have disappeared as a result of chemical combination, and one of the usual means by which this neutralization in properties is judged of, consists in observing the effect which is produced upon certain vegetable colours when mixed with a solution of the salt.

The blue colour of litmus, for example, is changed to red by the action of an acid, whilst the colour of litmus reddened by an acid becomes blue if it be mixed with an alkali. The yellow colour of turmeric is changed to brown when mixed with an alkali, but the yellow is restored if the alkali be caused to combine with an acid. A salt which affects neither the blue of litmus

nor the yellow of turmeric is said to have a neutral reaction. But chemists are in the habit of regarding many salts as neutral in composition which are not neutral in their action upon coloured tests. The basic properties of different metallic oxides vary considerably in intensity. Equal quantities of the same acid, according as it is neutralized by equivalent quantities of a weak base or of a strong one, will differ considerably in their action upon coloured tests: for example, 62 parts of nitric acid in combination with 39 parts of potassium furnish 101 of potassic nitrate ( $\text{KNO}_3$ ), which, when dissolved in water, does not affect the colour either of blue or of reddened litmus-paper. It is therefore neutral in its reactions upon coloured tests.

Salts of nitric acid in which 1 atom of a monad like potassium, sodium, or silver displaces the hydrogen in 1 atom of the acid  $\text{HNO}_3$ , or in which 1 atom of a dyad such as lead or copper displaces the hydrogen of 2 atoms of nitric acid ( $2\text{HNO}_3$ ), are regarded as neutral in composition, whatever may be their action upon vegetable colours. If, for instance, 223 parts of plumbic oxide ( $\text{PbO}$ ) be made to act upon 126 parts of nitric acid, plumbic nitrate and water will be formed;  $\text{Pb''O} + 2\text{HNO}_3 = \text{H}_2\text{O} + \text{Pb''2NO}_3$ , and the salt is neutral in composition, though if dissolved in water it reddens litmus, and has an acid reaction. The same thing is true, also, in the case of cupric nitrate ( $\text{Cu''2NO}_3$ ).

The change in the tint of the coloured test is therefore not to be regarded as an absolute proof of neutrality or acidity in the composition of a salt. The change of colour which the litmus experiences, even from a salt of neutral composition, is readily explained. Blue litmus is itself a species of salt, formed by the combination of the metals of one of the alkalies or earths with the oxion of a feeble vegetable acid which is naturally of a red colour, but which becomes blue when it is neutralized by an alkali. When a powerful acid, such as the nitric or the sulphuric, is mixed with this blue colouring matter, the oxion of the strong acid seizes upon the basyl which the litmus contains, and sets free the litmus acid, which appears of its natural red hue; but on the addition of an alkali the blue is restored by the reaction of the newly added base upon the litmus acid and the formation of the litmus salt of the alkali-metal. Again, if a salt with a strong oxion and a comparatively feeble basyl be mixed with the blue litmus, the strong oxion seizes upon a part of the basyl which is in combination with the litmus, and liberates the litmus acid, which appears of a more or less intense red, according as the basyl of the neutral salt has given up more or less of its oxion.

For analogous reasons it sometimes happens that a salt which is neutral in composition may exhibit characters in which the basyl preponderates to a greater or less extent. Common or dipotassic carbonate ( $K_2CO_3$ ) is neutral in composition, but it appears to be basic in its action upon the yellow colour of turmeric-paper, which it renders powerfully brown, and it immediately restores the blue tinge to reddened litmus. This ambiguity in the use of the word neutral, may, however, be entirely obviated by describing as *normal salts* the salts above-mentioned as neutral in composition; employing the term neutral solely with reference to the action of the body upon coloured tests; and in this sense these terms will be used hereafter.

(554) *Polybasic Acids—Acid Salts*.—If a quantity of oxalic acid be divided into two equal portions, one of which is dissolved in water, and mixed with a solution of potassic hydrate until the liquid becomes neutral in its reaction upon litmus, a salt is formed which, on evaporation, may be obtained crystallized in six-sided prisms, consisting of the normal or dipotassic oxalate, ( $K_2C_2O_4 \cdot H_2O$ ). If this salt be redissolved in water, and the second portion of oxalic acid be added to it, chemical union of the two bodies will occur; the liquid so obtained will be found to have a sour taste, to redden litmus powerfully, and on evaporation to yield a new salt, which crystallizes in rhomboidal prisms, containing exactly half as much potassium in proportion to the acid as the first salt; this is the hydropotassic oxalate, commonly known as the binoxalate, or acid oxalate, of potassium ( $KHC_2O_4 \cdot H_2O$ ); for  $K_2C_2O_4 \cdot H_2O + H_2C_2O_4 \cdot H_2O = 2(KHC_2O_4 \cdot H_2O)$ .

Again, if the normal or dipotassic sulphate ( $K_2SO_4$ ) be dissolved in hot sulphuric acid, tabular plates of a new, fusible, and strongly acid salt, will crystallize out as the liquid cools, and the hydropotassic sulphate, commonly called the bisulphate or acid sulphate of potassium ( $KHSO_4$ ) will be formed; for,  $K_2SO_4 + H_2SO_4 = 2KHSO_4$ . This salt contains only half the amount of potassium which is present in the normal sulphate. If an attempt be made to form a similar acid salt by dissolving potassic nitrate in nitric acid, the experiment will fail, for the nitre will be found to crystallize out unchanged.

The bodies now distinguished as acids, it must be remembered, are simply salts of hydrogen; and, from the experiments just described, it is apparent that there are certain acids in which their basic hydrogen admits of displacement by a metallic basyl in one proportion only, whilst there are other acids in which the hydrogen admits of displacement by a metal in two proportions, form-

ing two classes of salts, one of which is neutral in its reaction, the other is acid. Such acid salts consequently contain, in addition to the oxion and basyl, a certain quantity of hydrogen, as occurs, for instance, in the acid sulphate and the acid oxalate of potassium. This hydrogen is not to be regarded as present in the form of water of crystallization: it discharges a more important function, for it takes the place of one of the atoms of the metal on these occasions; and it is because the basylous properties of hydrogen are so feeble, that the acid character predominates to so great a degree in such salts.

Acids in the molecule of which but a single atom of hydrogen admits of displacement by an atom of a metallic monad such as potassium, are said to be *monobasic*. Of this description the hydrochloric acid  $\text{HCl}$ , the nitric,  $\text{HNO}_3$ , and the acetic,  $\text{HC}_2\text{H}_3\text{O}_2$ , acids are examples.

If, however, the molecule of the acid contains 2 atoms of hydrogen, susceptible of displacement by two atoms of a monad like potassium, or by one atom of a dyad like zinc, the acid is said to be *dibasic*, like the sulphuric,  $\text{H}_2\text{SO}_4$ , the oxalic,  $\text{H}_2\text{C}_2\text{O}_4$ , and the tartaric,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ , acids. Many of the vegetable acids belong to this class.

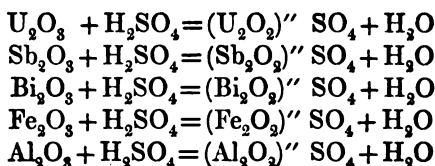
Again, if the molecule of the acid contains 3 atoms of hydrogen susceptible of displacement by 3 atoms of a monad like potassium or silver, or by one atom of a triad like bismuth, such an acid is said to be *tribasic*. Orthophosphoric acid,  $\text{H}_3\text{PO}_4$ , is a good instance of this kind; and among the organic acids the citric,  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ , may be mentioned.

Acids which allow the substitution of more than one atom of hydrogen by a corresponding number of atoms of a metallic monad (whether 2, 3, or 4 atoms) are said to be *polybasic*.

Ordinary nitre affords an instance of the formation of a normal salt by the action of the oxide of a metallic monad upon a monobasic acid ( $\text{KHO} + \text{HNO}_3 = \text{H}_2\text{O} + \text{KNO}_3$ ); whilst plumbic nitrate ( $\text{Pb}''2\text{NO}_3$ ) illustrates the case of a normal salt formed by the reaction of the protoxide of a dyad metal upon a monobasic acid ( $\text{Pb}''\text{O} + \text{HNO}_3 = \text{H}_2\text{O} + \text{Pb}''2\text{NO}_3$ ); and potassic sulphate affords an example of the formation of a normal salt by the reaction of the oxide of a monad metal with a dibasic acid ( $2\text{KHO} + \text{H}_2\text{SO}_4 = 2\text{H}_2\text{O} + \text{K}_2\text{SO}_4$ ). These three varieties include the most common forms of normal salt. When a dibasic acid acts upon the protoxide of a metallic dyad, a salt is formed similar to that obtained by the reaction of sulphuric acid upon calcic hydrate, where two atoms of hydrogen in the acid are

replaced by 1 atom of the dyad calcium;  $\text{Ca}''\text{H}_2\text{O}_3 + \text{H}_2\text{SO}_4 = 2\text{H}_2\text{O} + \text{Ca}''\text{SO}_4$ .

But numerous salts are known which are formed by the action of sesquioxides upon the acids. In certain cases the sesquioxides act upon the acids just as the protoxides do. For instance, the sesquioxides of antimony and uranium, as well as those of bismuth, iron, and aluminum, in certain circumstances yield a sulphate by the action of the two bodies in the proportions indicated in the following equations:—



These sulphates, however, with the exception of the first, are all insoluble; the oxide of uranium  $(\text{U}_2\text{O}_3)''$ , *uranyl*, as Péligré has termed it, has been isolated; indeed, it was for some years mistaken for metallic uranium, till Péligré showed it to be a compound, and obtained the metal itself. Bismuthyl  $(\text{Bi}_2\text{O}_3)''$  has also been procured, but the other oxides of the formulæ corresponding to uranyl have not as yet been isolated. The foregoing salts are generally regarded as basic salts, derived from the sesquioxides. Many of them may be conveniently represented either by the general formula  $\text{M}_2\text{O}_3\cdot\text{SO}_3$ , or they may, by trebling the formulæ just given above, be represented in the following manner; but they often retain water not indicated in the formulæ:—

Basic antimonious sulphate	...	...	$\text{Sb}_2\text{SO}_4\cdot 2\text{Sb}_2\text{O}_3$
„ bismuth	„	...	$\text{Bi}_2\text{SO}_4\cdot 2\text{Bi}_2\text{O}_3$
„ ferric	„	...	$\text{Fe}_2\text{SO}_4\cdot 2\text{Fe}_2\text{O}_3$
„ aluminic	„	...	$\text{Al}_2\text{SO}_4\cdot 2\text{Al}_2\text{O}_3$

In the majority of instances, when a dibasic acid, such as the sulphuric, acts upon a sesquioxide, such as alumina or ferric oxide, three atoms of the dibasic acid are required to form a normal soluble salt, in which case the metal becomes terequivalent, and two atoms of the metal are therefore equivalent to 6 atoms of hydrogen. For example,  $(\text{Al}''')_2\text{O}_3 + 3\text{H}_2\text{SO}_4$  yield  $3\text{H}_2\text{O} + (\text{Al}''')_2\text{SO}_4$ , and under these particular circumstances iron itself, instead of being biequivalent, as in the ferrous salts, becomes terequivalent in these ferric salts.  $(\text{Fe}''')_2\text{O}_3 + 3\text{H}_2\text{SO}_4$  yield  $3\text{H}_2\text{O} + (\text{Fe}''')_2\text{SO}_4$ ; thus affording an example of the remarkable fact of a metal possessing two different equivalents.

Other metals besides iron exhibit this power of assuming two



different equivalents: chromium and cerium, for example, in particular cases may be biequivalent, whilst in other cases they are undoubtedly terequivalent metals; for instance, they are biequivalent in—

Chromous chloride and sulphate	...	$\text{Cr}'\text{Cl}_2$ ; $\text{Cr}'\text{SO}_4$
Cerous chloride and sulphate	...	$\text{Ce}''\text{Cl}_2$ ; $\text{Ce}''\text{SO}_4$

and terequivalent in

Chromic chloride and sulphate	...	$\text{Cr}'''\text{Cl}_3$ ; $\text{Cr}'''\text{SO}_4$
Ceric chloride and sulphate	...	$\text{Ce}'''\text{Cl}_3$ ; $\text{Ce}'''\text{SO}_4$

In the protoxides and salts corresponding to them, these metals are biequivalent; whilst in the sesquioxides and the salts corresponding to them the metals are terequivalent. Tin, platinum, and palladium, again, in certain cases are biequivalent, in others quadrequivalent. This subject will be further considered in the opening chapter of the third volume of this work.

The normal salts derived from these different sesquioxides by the action of acids upon them have usually an acid taste, and redden litmus powerfully. This is well seen in the normal ferric and aluminic sulphates.

It is not necessary that the two or the three atoms of basyl which the salts of the dibasic or tribasic acids contain should consist of the same metal. Indeed, it has already been shown, in the case of the various phosphates, that several basyls may coexist in the same salt, in definite proportions. In disodio-dihydric pyrophosphate, for example ( $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ), 2 atoms of hydrogen supply the place of 2 atoms of sodium; and in the microcosmic salt ( $\text{Na}_2\text{H}_4\text{N}_2\text{H}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ ), we have a tribasic sodio-ammonio-hydric phosphate, where each of the three atoms of basyl differs from the others.

Now it frequently happens that hydrogen is one of the basyls present in the salt, and when such is the case, the salt, when dissolved in water, usually has a sour taste, and reddens litmus-paper strongly. It is in this way that the most common variety of acid salts is formed, such as the so-called binoxalate and the bisulphate of potassium already adverted to (p. 365). Cream of tartar, or, as it is often called, bitartrate of potash, offers another good illustration of this kind of salt.

Cream of tartar is a sparingly soluble crystallizable compound, of an agreeable acidulous taste; it consists of  $\text{KHC}_4\text{H}_4\text{O}_6$ , and is, in fact, a dibasic potassio-hydric tartrate: if now it be dissolved in hot water, and another equivalent proportion of caustic potash be added, the hydrogen is displaced by the second atom of potassium, all the acid taste disappears, and normal or dipotassic tar-

trate is produced ( $K_2C_4H_4O_6$ ), a salt which no longer affects the colour either of litmus or of turmeric paper. An equivalent quantity of potassic carbonate may be substituted for caustic potash with equal effect, as it will be decomposed, and the carbonic anhydride will be expelled with effervescence. Sodid carbonate may be substituted for potassic carbonate, but in this case a different salt, known as Rochelle salt, the sodio-potassic tartrate ( $KNaC_4H_4O_6 \cdot 4H_2O$ ) will be formed by the following reaction;  $NaHCO_3 + KHC_4H_4O_6 = H_2O + CO_2 + KNaC_4H_4O_6$ .

Acid salts are generally formed like cream of tartar, from a dibasic acid which has reacted with 1 atom only of a powerful monad base, while the place of the second atom of metal has been supplied by an atom of hydrogen; but they are not always so produced: an acid sulphate of potassium, which is anhydrous, may be obtained ( $K_2SO_4 \cdot SO_3$ ); and the acid chromate or bichromate of potassium ( $K_2CrO_4 \cdot CrO_3$ ) always occurs in the anhydrous form. Such salts have been distinguished from ordinary acid salts by the term *anhydro-salts*, or salts containing an anhydride.

(555) *Double Salts*.—The foregoing description of the polybasic acids has presented us with certain cases in which *double salts* are formed. There are several varieties of double salts. The most common are those which are produced by the union of two dissimilar metals with the same acid radicle or oxion. These varieties, however, are confined within certain limits. It is not possible to form double salts *ad libitum*, by bringing 2 equivalents of any acid in contact with 1 equivalent each of any two bases. Chemists assume that when two different metallic monads, such as sodium and potassium, combine with the same oxion in the proportion of 1 atom of each metal to form a double salt (like Rochelle salt), the acid in question is dibasic. The larger number of double salts which have been produced are thus formed by the combination of different metals with polybasic oxions. The so-called bicarbonates, binoxalates, and many other similar compounds, prove, on examination to be, as we have already shown, true double salts of this class, analogous to normal or neutral salts, in composition; but one-half of their basylous constituents consists of hydrogen. Some other considerations relating to the basicity of acids and to the polybasic acids will be more conveniently deferred until the nature of the organic acids has been discussed.

The formation of another remarkable series of double salts, particularly investigated by Graham, appears to be directly connected with the mode in which water attaches itself to certain

salts. In most cases the water of crystallization may be expelled from a salt by exposing it to a temperature not exceeding that of boiling water. This, however, does not always happen: sometimes all the water of crystallization may thus be expelled with the exception of a single atom, which requires a much higher heat for its expulsion, although in these cases it does not appear to act in any degree as a base. Under these circumstances it was found that this last atom of water might readily be displaced by adding to the salt an equivalent of certain anhydrous salts. An excellent illustration of such a method of the formation of double salts is afforded in the case of a certain class of the sulphates. All the sulphates of metals isomorphous with magnesium are capable of forming double salts of this nature with some anhydrous sulphate not isomorphous with this class—such, for instance, as potassic sulphate.

When magnesian sulphate ( $\text{MgSO}_4 \cdot \text{H}_2\text{O} \cdot 6\text{H}_2\text{O}$ ) is heated to  $100^\circ \text{C}$ ., six out of the seven atoms of water are expelled, but the seventh atom is retained until the temperature is raised considerably. If, however, magnesian sulphate and potassic sulphate be separately dissolved in water in equivalent proportions, mixed while hot, and allowed to crystallize, a new double salt ( $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ) is deposited, having the same crystalline form as magnesian sulphate, but it contains only 6 atoms of water of crystallization. The seventh atom has been displaced by the potassic sulphate, and this portion of water has hence been termed by Graham, constitutional, or *saline water*.

There is another well-known variety of double salts, in which it is not necessary that the component salts should be formed from oxides of the same class, or even contain a similar number of equivalents of the radicle of the acid. In this way sulphates formed from sesquioxides often unite with the sulphates formed from protoxides to produce well-characterized double salts: a striking example of this kind is afforded in the important tribe of alums. Common alum consists of a combination of potassic with aluminic sulphate and water of crystallization ( $\text{KAl}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ ): numerous other salts, having the same crystalline form, and of similar composition, might be mentioned.

There are a few instances of two different oxions or acid radicles being united to one basyl, but they are neither sufficiently numerous nor important to merit lengthened notice; they are more frequently met with among natural than artificial combinations.

Instances are common in which two different haloid salts

unite with each other; compounds of this description are most usual between the chlorides, iodides, and bromides of the less oxidizable metals with those of the metals contained in the alkalis and earths: the potassio-platinic chloride ( $2\text{KCl}, \text{PtCl}_4$ ) and the potassio-mercuric iodide ( $2\text{KI}, \text{HgI}_2$ ) are good instances of such compounds. Bonsdorff proposed to consider these compounds in the light of salts in which the chloride or iodide of the electronegative metal (platinum, gold, &c.) acted the part of an acid towards the electropositive chloride (chloride of potassium, sodium, &c.); but this view is not tenable. Such salts are never resolved by electric action into their constituent chlorides, and the acid reaction of the higher chlorides is not neutralized or modified by combination with the chlorides of the alkali-metals; in fact, the constituent chlorides themselves are salts.

Many double salts may be formed by fusion with each other, though they cannot be procured by the usual method of crystallization from a solution containing equivalent quantities of the two salts. Sodid chloride, for example, may be melted with an equivalent amount of calcic, strontic, or baric chloride; and in each case a compound salt is obtained, which has a much lower fusing-point than either of its component chlorides in a separate form; but the double salt is decomposed when it is dissolved in water.

(556) *Subsalts*.—A very different series of saline compounds still remains for consideration, and in these the proportion of base predominates over that of the acid; they are usually designated *basic salts*, or subsalts. The theory of the formation of these compounds is very imperfect. In many cases subsalts may be compared to salts which contain water of crystallization, the atoms of base in excess being assumed to be attached to the normal salt in a manner analogous to that by which the water of crystallization is retained in ordinary instances.

The tendency to the formation of subsalts is limited to certain acids and bases. It is indeed one of the peculiarities of the monad bases, such as the alkalis, and the oxides of silver and thallium, that they do not form basic salts; oxides of the dyads, such as the oxides of copper, lead, mercury, and zinc, have a strong tendency to do so, while the oxides of the triads, when basic, such as the sesquioxides of antimony and bismuth, have a still greater propensity to form basic salts. No general rule can be laid down for the acids, but among the common acids, those which most frequently form basic salts are the sulphuric, nitric, carbonic, and acetic acids.

Among basic sulphates, for example, are the following :—

Brochantite ... ..	$\text{CuSO}_4, 3\text{CuOH}_2\text{O}$
Tribasic cupric sulphate ... ..	$\text{CuSO}_4, 2\text{CuOH}_2\text{O}$
Turpeth mineral ... ..	$\text{HgSO}_4, 2\text{HgO}$ .

Among basic nitrates are,

Dibasic plumbic nitrate ... ..	$\text{Pb}_2\text{NO}_3, \text{PbO}, \text{H}_2\text{O}$
Tetrabasic cupric nitrate ... ..	$\text{Cu}_2\text{NO}_3, 3\text{CuOH}_2\text{O}$
Mercurous subnitrate ... ..	$3(\text{Hg}_2, 2\text{NO}_3), \text{Hg}_2\text{O}, \text{H}_2\text{O}$
De Marignac's do. ... ..	$3(\text{Hg}_2, 2\text{NO}_3), 2\text{Hg}_2\text{O}, \text{H}_2\text{O}$ .

The following are instances of basic acetates :—

Verdigris ... ..	$\text{Cu}_2\text{C}_2\text{H}_3\text{O}_2, \text{CuO}, 6\text{H}_2\text{O}$
Tribasic cupric acetate ... ..	$2(\text{Cu}_2\text{C}_2\text{H}_3\text{O}_2), 4\text{CuO}, 3\text{H}_2\text{O}$
Tribasic plumbic acetate ... ..	$\text{Pb}_2\text{C}_2\text{H}_3\text{O}_2, 2\text{PbO}, \text{H}_2\text{O}$
Hexabasic plumbic acetate ... ..	$\text{Pb}_2\text{C}_2\text{H}_3\text{O}_2, 5\text{PbO}, \text{H}_2\text{O}$ .

As examples of basic carbonates, we give,

Malachite ... ..	$\text{CuCO}_3, \text{CuOH}_2\text{O}$
Blue carbonate of copper ... ..	$2\text{CuCO}_3, \text{CuOH}_2\text{O}$
White lead ... ..	$2\text{PbCO}_3, \text{PbOH}_2\text{O}$ .

Just as we have polybasic acids, so are there polyacid basyls—basyls, that is, such as the dyads or triads, which require more than one atom of a monobasic oxion for their saturation. This is the case, for example, with the metals of the alkaline earths; but as yet the class of double salts, which they no doubt compose, has been scarcely examined.

(557) *Oxychlorides, &c.*—A class of compounds which resemble the subsalts more than any others, is presented to us in the bodies termed oxychlorides, oxyiodides, and oxycyanides of the metals. In these compounds, one atom of the chloride, of the iodide, or of the cyanide of a metal is united with one or more atoms of the oxide of the same metal. Turner's yellow, which is an oxychloride of lead ( $\text{PbCl}_2, 7\text{PbO}$ ), is a well-known commercial article belonging to this class. Such combinations usually occur between oxides and chlorides or iodides of metals the pure chlorides or iodides of which never form any but anhydrous crystals.

Some salts enter into combination with other bodies, and form compounds which are in many respects anomalous; such for instance are the compounds of ammonia with many dry salts: 2 atoms of argentic chloride will in this manner absorb 3 atoms of ammonia. Many of the salts of copper exhibit a similar power (622).

## CHAPTER XII.

## GROUP I.—METALS OF THE ALKALIES.

Metal.	Symbol.	Atomic weight.	Atomic volume.	Specific heat.	Fusing point.		Specific gravity.	Electric conductivity. 68—71 F°.
					°C.	°F.		
Cæsium ...	Cs	133						
Rubidium	Rb	85.3	56.1		38.5	101.3	1.52	
Potassium	K	39.1	44.96	0.16956	62.5	144.5	0.865	20.85
Sodium ...	Na	23	23.60	0.29340	97.6	207.7	0.972	37.43
Lithium ...	L	7	11.80	0.94080	180.0	356.0	0.593	19.00

THE metals of this class are soft, easily fusible, and volatile at high temperatures; they furnish several oxides, of which only one is basic. This oxide is caustic, and extremely deliquescent: the hydrate cannot be decomposed by ignition; it absorbs carbonic acid with avidity. The carbonates are soluble, so are the sulphides and hydrosulphates of the sulphides (see p. 329).

§ I. POTASSIUM (Kalium) [ $K' = 39.1$ ] *Sp. Gr.* 0.865;  
*Fusing-pt.* 144° 5 (62° 5 C.)

*Native Compounds which contain Potassium.*

Alum . . . .  $KA_2SO_4, 12H_2O$ .

Felspar . . . .  $(KNa)'_2O, Al_2O_3, 6SiO_2$ .

Biaxal mica . .  $(K_2O, 3[(AlFe)''', O_2] 6SiO_2)$ .

(558) *Symbols of Mixtures of Isomorphous Compounds.*—The formulæ employed above for felspar and mica require explanation, as the principle of notation adopted in these cases will be applied hereafter to the formulæ of a large number of minerals.\*

It often happens that isomorphous bases displace each other in the same mineral without altering its form or mineralogical characters, or even without altering its general chemical formula. Mica, for example, may be regarded as a compound of 1 atom of a silicate of a protoxide of a metal with 3 atoms of a different silicate of a sesquioxide of a different metal. Let M stand for

\* The formulæ of the silicates are so complex, and the true function of silica in combination is at present so ill defined, that I have throughout formulated them as containing silica in combination with the bases.

the metallic base of the protoxide, N for the metallic base of the sesquioxide; the general formula for mica may then be expressed thus:—



Now the components of potash-mica are principally silicate of potash and silicate of alumina, the potash being the metallic protoxide and the alumina being the metallic sesquioxide; but the sesquioxides of iron, manganese, and chromium are also isomorphous with alumina: these compounds frequently displace a portion of the alumina from its combinations, and this is especially the case with the sesquioxide of iron. The peculiarity of isomorphous metals, when they displace each other, is this—that the displacement is liable to occur in any possible proportion; for example, in different specimens of mica the relative proportions of iron and aluminum are liable to great variations; this arises from the fact that the ferric silicate and aluminic silicate which are isomorphous, may be mixed in any conceivable proportion, and will crystallize together without altering the form of the mineral. The same fact may also be represented by stating that they may vary indefinitely in amount, provided only that the quantity of the two metals taken together in any one specimen furnishes such a proportion of a metallic sesquioxide as is equivalent to the silica in that portion of the mineral; that is to say, that the two proportionals of metal required for combination with the 3 proportionals of oxygen in the sesquioxide, may either consist wholly of aluminum, or a *small but indefinite* proportion of the aluminum may have its place supplied by a *small but equivalent* quantity of iron, or a large proportion of the aluminum may have its place supplied by a corresponding and equivalent proportion of iron.

Now the method of notation adopted in the preceding formulæ is employed to indicate precisely this—that the proportions of the two or more metals, the symbols of which are bracketed together, thus,  $(\text{AlFeMn})'''_2\text{O}_3$ , are liable to vary within any conceivable limits, provided that the united amount of all the metals so bracketed be exactly sufficient to form a true sesquioxide with the three proportionals of oxygen.

In like manner, in the case of the potassium in felspar, the place of part of the potassium may be supplied by sodium; but the proportions of the two taken together require exactly the same amount of oxygen, and consequently saturate the same proportion of silica, that 1 atom of potash alone would have required.

This frequent partial displacement of one isomorphous metal by another in native crystallized minerals, renders much caution necessary in interpreting the results of an analysis. The difficulty of fixing the formula of a mineral of course increases with the complexity of its composition, and it is with the silicates especially that these difficulties are experienced. It is usual, when the analytical operations are completed, to ascertain the proportion of oxygen in the silica, then the proportion of oxygen contained in the sesquioxides, and lastly the quantity of oxygen in the protoxides; because, however much the proportions of the different metals may vary in different specimens of the same mineral, the ratio of the oxygen in both sets of bases to the oxygen in the silica remains uniform. In felspar, for instance, if the proportion of oxygen in the silica be taken as 12, that in the sesquioxide of aluminum is 3, and that in the protoxide of potassium or sodium is 1.

(559) POTASSIUM.—This remarkable metal was discovered by Davy, in the year 1807, and its isolation marks an important era in the progress of philosophical chemistry. The alkalies and the earths had long been suspected to be compound bodies, but up to that period they had resisted all attempts to decompose them. When once potassium, however, had been separated from its compounds, and potash had been proved to be an oxide of this metal, the decomposition of the other alkalies and earths followed as a necessary consequence: more correct ideas upon fundamental points of chemical theory were introduced; new methods of research were placed within reach of the analytical chemist, and potassium itself, from its powerful attraction for oxygen, became an important addition to the reagents of the laboratory.

*Properties.*—Potassium is a bluish-white metal, which is brittle, and has a crystalline fracture at  $0^{\circ}$  C.; at temperatures a little above this it is malleable: at  $15^{\circ}$  C. it is soft; as the temperature rises it becomes pasty, and at  $144^{\circ} \cdot 5$  ( $62^{\circ} \cdot 5$  C.) it is completely liquid. Whilst in the soft condition, two clean surfaces of the metal admit of being welded together like iron; at a red heat it may be distilled, and it yields a beautiful green vapour. Potassium is light enough to float in water, having a specific gravity of only 0.865. If exposed to the air, even for a few minutes only, it becomes covered with a film of oxide: when heated to its point of volatilization it bursts into flame, and burns with great violence. The powerful attraction of potassium for oxygen is seen on throwing the metal into water, in which



case part of the water is immediately decomposed: each atom of potassium displaces half the hydrogen of an atom of water, and potassic hydrate is formed,  $2\text{H}_2\text{O} + \text{K}_2 = 2\text{KHO} + \text{H}_2$ , while the escaping hydrogen carries with it a small portion of the volatilized metal, and taking fire from the heat evolved, burns with a beautiful rose-red flame; the metal melts and swims about rapidly upon the water, and finally disappears with an explosive burst of steam, as the globule of melted potassic hydrate which is formed during its oxidation becomes sufficiently cool to come into contact with the water. Potassium decomposes nearly all gases which contain oxygen, if it be heated in contact with them; and at a high temperature it will remove oxygen from almost all bodies into the composition of which that element enters. It becomes necessary therefore to preserve the metal either in exhausted hermetically sealed glass tubes, or under the surface of some liquid, like naphtha, which does not contain oxygen. At a heat short of redness potassium absorbs hydrogen and becomes converted into a greyish mass ( $\text{HK}_4$  ?); but if more strongly heated, the hydrogen is again expelled. Potassium enters into direct combination with the halogens and with sulphur, selenium, and tellurium, burning vividly when heated with them. It likewise absorbs carbonic oxide with facility when heated moderately in it, or when the vapour of potassium is allowed to condense slowly in an atmosphere of the gas: a black mass is thus formed from which the metal cannot be recovered: it furnishes potassic rhodizionate when treated with water, and occasions considerable waste in the ordinary method of preparing potassium.

(560) *Preparation*.—1. Davy originally obtained potassium by decomposing a fragment of caustic potash (which had become slightly moistened upon its surface by exposure to the air for a few minutes) by the current of a voltaic battery of 200 or 250 pairs of plates, 6 inches (15 centim.) square, on Wollaston's construction. (*Phil. Trans.* 1808, 4). The dry hydrate is an insulator, but a trace of moisture confers upon it a sufficient degree of conducting power; under such circumstances globules of metallic potassium are separated at the negative wire, and may be preserved under naphtha. They burn vividly in air, leaving an intensely alkaline residue. This method of procuring the metal, however, furnishes it only in very small quantity, and is difficult and expensive.

2.—Gay-Lussac and Thénard, in 1808, invented a method by which potassium may be obtained by purely chemical means in greater abundance. Iron turnings were heated to whiteness in a curved gun-barrel, which was covered with a clay lute, to pre-

serve it from the action of the air at a high temperature, and melted caustic potash was allowed to pass slowly over the ignited iron; decomposition ensued, the iron combined with the oxygen, and potassium along with hydrogen passed forwards, the potassium condensing in a copper receiver which was kept cool.

3.—The process by which potassium is now obtained consists in decomposing its carbonate by charcoal, a plan originally invented by Curaudau, and improved by Brunner. This operation has been carefully studied by Mareska and Donny (*Ann. de Chimie*, III. xxxv. 147). In order to ensure a successful result, attention to a number of minute precautions is requisite. The material which is best adapted to its preparation is the potassium salt of some vegetable acid, which, when decomposed by heat in a vessel from which air is excluded, leaves a large quantity of carbon.

For this purpose hydropotassic tartrate (crude tartar) is preferred. About 3 kilos. or 7 lb. of this substance is placed in a capacious iron crucible furnished with a cover, and ignited till it ceases to emit combustible vapours. A porous mass of potassic carbonate, intimately mixed with very finely divided carbon, is thus obtained: this is rapidly cooled by moistening the exterior of the crucible with cold water; the charred mass, when cold, is broken up into lumps of about the size of a hazel-nut, and quickly introduced into a wrought iron retort. This retort is usually made of one of the iron bottles in which mercury is imported; it is introduced into a furnace, *a*, as shown at *b*, fig. 337, and placed horizontally upon supports of fire-brick, *f f*; a wrought-iron tube, *d*,  $4\frac{1}{2}$  inches (or 11 centimetres) long, serves to convey the vapours of potassium produced during the distillation into a receiver, *e*, which it is found most advantageous to construct of the form shown on an enlarged scale in fig. 338. It consists of two pieces of

FIG. 337.

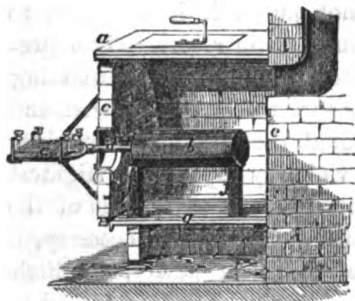
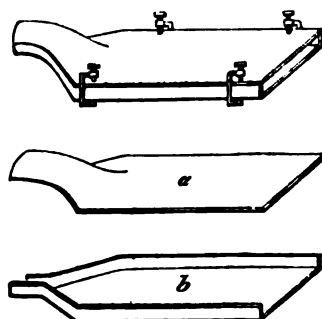


FIG. 338.



wrought iron, *a*, *b*, which are fitted closely to each other, so as to form a shallow box only a quarter of an inch ( $6^{\text{mm}}$ ) deep, and are confined in their places by clamp screws: the iron plate should be  $\frac{1}{2}$  in. ( $4^{\text{mm}}$ ) thick, 12 in. ( $30^{\text{cm}}$ ) long, and 5 inches (or  $12^{\text{cm}}$ ) wide; the receiver is open at both ends, the socket fitting upon the neck of the iron retort. The object of preparing the receiver of this particular form is to ensure the rapid cooling of the potassium, and so to withdraw it from the action of the carbonic oxide which is disengaged during the whole process. Before this receiver is connected with the tube, *d*, the fire is

slowly raised until the retort attains a dull red heat; powdered vitrified borax is then sprinkled over its exterior; the borax melts, and forms a coating which protects the metal from oxidation. The heat is then urged until it becomes very intense. A mixture of coke and charcoal forms a fuel well adapted to this purpose: care should be taken that the temperature of the furnace be raised as equally throughout every part as possible. When a full reddish-white is attained, vapours of potassium begin to appear, and burn with a brilliant flame: the receiver is now adjusted to the iron neck of the retort, which is not allowed to project more than a quarter of an inch ( $6^{\text{mm}}$ ) through the iron plate which forms part of the front wall, *c*, of the furnace, lest the tube should become obstructed by the accumulation of solid potassium. Should any obstruction occur, it must be removed by thrusting in an iron rod; if this fails, the fire must be immediately withdrawn; this is readily effected by removing the fire bars, *g*, from the furnace, with the exception of two which support the retort; the fuel thus falls into the ashpit. The receiver is kept cool by the application of a wet cloth upon its exterior. When the operation is complete, the receiver with the potassium is removed, and instantly plunged into a vessel of rectified Persian naphtha, provided with a cover. The vessel is kept cool by immersion in water. When this apparatus is sufficiently cold, the potassium is detached, and preserved under naphtha.

In order to obtain the maximum produce of potassium, it is necessary that the mixture of potassic carbonate and carbon should contain 1 atom of the carbonate to 2 of carbon, or 138 parts of the carbonate by weight to 24 of carbon. Upon the application of heat the mixture is wholly converted into carbonic oxide and potassium;  $\text{K}_2\text{CO}_3 + \text{C}_2 = \text{K}_2 + 3\text{CO}$ . The charge usually yields about one-fourth of its weight of crude potassium, some loss during the process being inevitable. Mareska and Donny found this loss to amount to about one-third of the entire quantity of the metal contained in the charge.

The potassium so obtained is not pure; it is necessary to subject it to a second distillation in an iron retort. This precaution is *essential*; for, if it be neglected, a black detonating compound is speedily formed by exposure to the atmosphere, and is even produced spontaneously, although the metal be kept under naphtha; this substance explodes violently upon the slightest friction. The purified metal amounts to about two-thirds of the quantity operated on. A third distillation may be necessary, if the potassium be required in a state of perfect purity. A little impure potassium almost always remains in the tube attached to the retort; and in order to prevent the possibility of the formation of the detonating compound already mentioned, it is best to detach this tube as soon as it is cold, and to immerse it in water.

(561) OXIDES OF POTASSIUM.—Potassium forms three well-established compounds with oxygen; a basic oxide, which constitutes potash, and furnishes the salts of the alkali; and two other oxides which do not form corresponding salts with acids. A blue

suboxide appears also to be formed upon the surface of the metal during its gradual oxidation in dry air.

	K.	O.
Potash ... .. $K_2O$	= 94.2 or 82.97	+ 17.03 = 100
Deutoxide of potassium $K_2O_2$	= 110.2 „ 70.08	+ 29.02 = 100
Peroxide of potassium $K_2O_4$	= 142.2 „ 54.93	+ 45.07 = 100.

*Percxide of potassium, Dipotassic tetroxide* ( $K_2O_4 = 142.2$ ; Harcourt, *Q. J. Chem. Soc.* xiv. 267).—This substance is formed when potassium is heated gently in a current of dry air; the operation must be completed in a current of dry oxygen gas: if formed at a temperature of  $536^\circ$  ( $280^\circ$  C.), it slowly cakes together, but below that temperature it furnishes a powder of a chrome-yellow colour. It absorbs moisture rapidly when exposed to the air, and is decomposed by water with extrication of oxygen and formation of a solution of the oxide ( $K_2O$ ).

(562) *Dipotassic oxide, Potash* ( $K_2O = 94.2$ ).—This compound can be procured in an anhydrous form by oxidating potassium in thin slices, in air perfectly free from moisture and carbonic anhydride; or by heating potassium with an equivalent quantity of the hydrate, when hydrogen is expelled and pure potash is formed,  $2KHO + K_2 = 2KKO = H_2$ . It is white, very deliquescent, and caustic; when moistened with water it becomes incandescent: after it has thus become hydrated, no degree of heat is sufficient to expel the water. Anhydrous potash fuses at a red heat, and is volatilized at a high temperature. For most purposes the presence of water is immaterial, potash is therefore generally procured in the state of hydrate, in which form it may be obtained without difficulty.

*Potassic hydrate, or Caustic potash* ( $KHO = 56.1$ ; *Sp. Gr.* 2.2; *Comp.* in 100 parts  $K_2O$ , 83.94;  $H_2O$ , 16.06) is prepared by dissolving potassic carbonate, of which the *pearlash* of commerce is an impure variety, in 10 or 12 times its weight of water, and adding to the boiling solution a quantity of caustic lime equal in weight to half the potassic carbonate used; the lime should be slaked, made into a thin paste with water, and added in small portions at a time, so that the liquid may be maintained at the boiling point: a crystalline calcic carbonate is precipitated, and potassic hydrate remains in solution;  $K_2CO_3 + CaH_2O_2$  giving  $2KHO + CaCO_3$ . After decantation from the precipitate, the liquid is evaporated rapidly in a clean iron or silver basin, till when the heat is raised nearly to redness, it flows without ebullition, like oil: it is then either cast into cylinders in a metallic mould, or is poured upon a cold stone slab, and solidifies on cooling. Caustic potash may also be obtained crystallized in acute rhombohedrons, ( $KHO, 2H_2O$ ), from a hot concentrated aqueous solution.

Caustic potash is one of the most indispensable reagents to the chemist. It is therefore necessary that he should be able readily to ascertain its purity, and if needful prepare it for himself: when required pure, hydropotassic carbonate (commonly known as bicarbonate,  $\text{KHCO}_3$ ), in crystals, may be decomposed in the manner above described, by means of lime obtained from black marble. The impurities which occur most frequently in ordinary caustic potash are carbonates, sulphates, chlorides, and silicates of calcium, aluminum, iron, and lead, and peroxide of potassium. If pure, it is perfectly soluble in water without effervescence; a diluted solution gives no precipitate with baryta-water, showing the absence of carbonates and sulphates: it yields no precipitate with ammoniac oxalate, showing the absence of calcic salts. On neutralizing it with nitric acid, argentic nitrate gives no precipitate, showing the absence of chlorine. Freedom from iron or metallic impurities is shown by the absence of any precipitate on the addition of hydro-ammoniac sulphide ( $\text{H}_4\text{NHS}$ ). Caustic potash, when pure, is wholly soluble in alcohol, the impurities above mentioned remaining undissolved. Common potash is therefore often purified by forming a solution of it in alcohol, and boiling down to dryness in a silver vessel, till it flows tranquilly; the alcohol is thus expelled, the melted hydrate is poured off upon a silver plate from the black crust which forms over its surface, and when cold it is broken up and placed in a well-closed bottle.

A dilute solution of pure potash may be readily obtained by adding a hot solution of baric hydrate to a solution of potassic sulphate, until the liquid gives no further precipitate either with baryta or with potassic sulphate;  $\text{K}_2\text{SO}_4 + \text{BaH}_2\text{O}_2 = \text{BaSO}_4 + 2\text{KHO}$ .

Potassic hydrate, after fusion, is a hard, greyish-white substance: it absorbs both moisture and carbonic anhydride rapidly from the air; it is soluble in about half its weight of water, with the extrication of considerable heat; it is likewise soluble in alcohol to an almost equal extent. Caustic potash has a peculiar nauseous odour, and an acrid taste; it is a powerful cautery, and quickly destroys both animal and vegetable matters; for this reason its solution cannot be filtered except through pounded glass or sand, and is always best clarified by allowing the impurities to subside, and then decanting the clear liquid. The solution should be preserved in glass bottles into the composition of which no oxide of lead enters, as the solution gradually dissolves this oxide out of the glass. It also attacks vessels even of green glass and of porcelain when heated in them.

The following table gives approximatively the proportion of

anhydrous potash contained in 100 parts by weight of solutions of the alkali of various densities :—

*Strength of Solutions of Potash (Dalton).*

Sp. gr.		K <sub>2</sub> O in 100 parts.	Sp. gr.		K <sub>2</sub> O in 100 parts.
1'60	...	46'7	1'33	...	26'3
1'52	...	42'9	1'28	...	23'4
1'47	...	39'6	1'23	...	19'5
1'44	...	36'8	1'19	...	16'2
1'42	...	34'4	1'15	...	13'0
1'39	...	32'4	1'11	...	9'5
1'36	...	29'4	1'06	...	4'7

The *Liquor Potassæ* of the Pharmacopœia contains nearly 6 per cent. of the solid hydrate, and has a sp. gr. of 1'058. The concentrated solution used for organic analysis may be obtained by dissolving 1 part of the hydrate in 3 parts of water.

At a high temperature potassic hydrate is wholly volatilized; consequently the water cannot be expelled from this hydrate by the mere application of heat. Its chemical attractions are so powerful that few vessels are found capable of resisting its action; those which contain silica are decomposed by it, and platinum itself is oxidized when heated in contact with it: gold and silver resist it better. Caustic potash decomposes the fixed oils, and converts them into soluble soaps: when fused with siliceous minerals it displaces the bases, and combines with the silica, forming potassic silicate. Potassic salts are extensively employed in the arts: to the soap-boiler and the glass-maker they are indispensable; the nitrate enters largely into the manufacture of gunpowder; and others of its salts in greater or less quantity furnish important aids to a variety of processes employed in the manufactures of the country. In the laboratory, caustic potash is in constant use for absorbing acid gases, such as carbonic acid, and for separating the metallic oxides from solutions of their salts, since owing to the powerful attraction of the alkali for acids, it readily decomposes the salts of all the metals which produce oxides insoluble in water. Salts of potash also constitute in small proportion, a necessary article of food; as according to Liebig the prolonged withdrawal of these compounds is the cause of scurvy; and they form a necessary constituent in antiscorbutic remedies.

Compounds of potassium are present in small proportion in all fertile soils, the grand reservoirs of this alkali-metal being the different varieties of clay, which contain 2 or 3 per cent. of it,

derived from the disintegration of felspar, in which silicate it exists in the proportion of from 10 to 12 per cent., and certain kinds of mica, which yield 5 or 6 per cent.: besides these numerous other silicates contain potash in small proportion. By exposure to the air and atmospheric vicissitudes, these rocks become gradually disintegrated; their soluble constituents, potash amongst the number, are taken up by the water which falls upon the earth's surface, and are assimilated by the plants which spring from its bosom; they accumulate it, especially in the leaves, young shoots, and succulent parts. Owing to this circumstance large quantities of potash may be obtained with facility: dried brushwood is incinerated, and the remaining ash, which seldom constitutes more than 1 per cent. of the dry wood, contains the potassium in the form of carbonate: the salt is extracted by water from the insoluble portions. M. Merle now extracts considerable quantities of potassic chloride from the mother-liquors of sea-water by a modification of the method of Balard (p. 407). Much potash accumulates as an organic salt in the fleece of the sheep and is wasted. Maumené and Rogelet collected this potassic salt by simply washing, and evaporating the wash water. A fleece weighing 4 kilos., or 9 lb., contains about 7 ounces (200 grammes) of pure potash, of which they consider nearly 6 oz. is recoverable. A good deal of the potash which is carried off the land cultivated for beet-root is now recovered by suitable treatment of the waste after the sugar has been extracted.

Messrs. Ward and Wynants a few years ago contrived a method of extracting potash from felspar in the form of carbonated or of caustic alkali, which, if commercially successful, will materially alter the source of supply of this alkali. In this process the felspar is ground to a fine powder, and mixed with a suitable quantity of chalk, slaked lime, and fluorspar. The materials are fritted in a furnace, at a heat about sufficient to fuse silver, the mixture not being allowed really to melt. The chalk during ignition evolves carbonic anhydride; it thus mechanically preserves the porosity of the mass, and facilitates the extraction of the soluble products. The mass obtained is then lixiviated, and rendered caustic by the addition of slaked lime. The proportion of lime required is indicated by the following formulæ, supposing the materials to be employed in a pure state:— $(K_2O_3SiO_2, Al_2O_3, 3SiO_2) + 7\frac{1}{2}CaO + CaF_2$ .—(*Hofmann's Jury Report*, 1862, p. 51.)

(563) SULPHIDES OF POTASSIUM.—Potassium takes fire readily and burns with brilliancy when heated in the vapour of sulphur. It combines with this element in not less than 4 and possibly in

5 different proportions,  $K_2S$ ?,  $K_2S_2$ ,  $K_2S_3$ ,  $K_2S_4$ , and  $K_2S_5$ . Owing to this circumstance, the reactions which occur when sulphur is heated with caustic or carbonated potash are somewhat complicated; but they are now well understood, and may be traced without difficulty.

*Dipotassic sulphide, or Protosulphide of potassium* ( $K_2S$ ).—Some doubt exists as to the possibility of forming this compound. The usual directions are to heat potassic sulphate in a current of dry hydrogen, or to mix the sulphate intimately with finely powdered charcoal, and ignite in covered vessels. Bauer, however (*Chem. Gaz.* 1858, 468), finds that the result is not that usually represented by the equation,  $K_2SO_4 + 4H_2 = K_2S + 4H_2O$ , but that a mixture of free alkali and a variable amount of one of the higher sulphides of potassium is the result. The residue obtained has a reddish-yellow colour; it is deliquescent, and acts powerfully upon the skin as a caustic. When a current of sulphuretted hydrogen is transmitted through a solution of caustic potash it is rapidly absorbed; and if the gas be allowed to pass till the liquid is completely saturated, the compound KHS will be obtained in solution. This solution is colourless when first prepared, but if exposed to the air it quickly absorbs oxygen, and acquires a yellow colour, owing to the formation of the sulphide  $K_2S_2$ ;  $4KHS + O_2 = 2K_2S_2 + 2H_2O$ . It is usually stated, and probably with truth, that if a solution of potash be divided into two equal portions and one be converted into the hydropotassic sulphide (KHS), and be then mixed with the other half of the solution of potash, a solution of pure dipotassic sulphide will be obtained,  $KHS + KHO$  becoming  $K_2S + H_2O$ . It is possible, however, that this is not so; but that both the caustic and potash and the double sulphide remain unaltered in the liquid. On the addition of a stronger acid sulphuretted hydrogen is given off abundantly, and this would occur whichever view were correct, no sulphur being deposited; for  $K_2S + H_2SO_4 = H_2S + K_2SO_4$ , and  $KHS + KHO + H_2SO_4 = H_2S + H_2O + K_2SO_4$ .

If potassic sulphate be mixed in fine powder with half its weight of lamp-black, and heated in a covered crucible, the sulphate is reduced to the sulphide ( $K_2S$ ), which remains in a finely divided state mixed with the excess of charcoal, and yields a *pyrophorus*, or compound which takes fire spontaneously in the air, owing to the heat emitted by its rapid absorption of oxygen.

The *Disulphide*, or *Dipotassic disulphide* ( $K_2S_2$ ) may be formed by exposing an alcoholic solution of KHS to the air till it begins to become turbid, and evaporating to dryness *in vacuo*. It fuses easily, and is of an orange colour.

The *Sesquisulphide* (*tersulphide* formerly) ( $K_2S_3$ ) is obtained pure by passing the vapour of carbonic disulphide over ignited potassic carbonate so long as any gas makes its escape: carbonic anhydride and carbonic oxide are produced,



as follows:  $2K_2CO_3 + 3CS_2 = 2K_2S_3 + 4CO + CO_2$ . In the old process of making *liver of sulphur*, 69 parts of dry pearlash are fused with 40 parts of sulphur; the resulting yellowish-brown mass consists of 3 atoms of sesquisulphide and 1 atom of potassic sulphate: part of the carbonate in this case yields oxygen to one portion of the sulphur, and forms sulphuric acid, as shown in the annexed equation:  $4K_2CO_3 + 5S_2 = K_2SO_4 + 3K_2S_3 + 4CO_2$ .

A *dipotassic tetrasulphide* ( $K_2S_4$  or  $K_2SS_3$ ) corresponding to the sulphite ( $K_2SO_3$ ) may be formed by reducing potassic sulphate by the vapour of carbonic disulphide.

*Dipotassic pentasulphide*, or *persulphide* ( $K_2S_5$  or  $K_2SS_4$ ) corresponding to the sulphate ( $K_2SO_4$ ) is formed by boiling a solution of any of the preceding sulphides with excess of sulphur till saturated: or by fusing any of the dry sulphides with an excess of sulphur; the excess of sulphur separates and floats above the sulphide, which has a dark liver-brown colour; it is deliquescent, and forms a deep yellow solution in water.

All these sulphides have an alkaline reaction to test-paper, and an odour of sulphuretted hydrogen more or less distinct. On the addition of a stronger acid they are decomposed with extrication of sulphuretted hydrogen, attended, in the case of all but the lowest sulphide, by the precipitation of white, finely divided sulphur. On adding the persulphide to an excess of hydrochloric acid of sp. gr. about 1.1, the persulphide of hydrogen (429) is separated as an oily liquid. By exposing solutions of the higher sulphides to air, they become colourless, potassic hyposulphite is formed, and the excess of sulphur is separated. When a solution of caustic potash is boiled with sulphur, a decomposition ensues similar to that which occurs when potassic hydrate and sulphur are fused together; a deep reddish-yellow liquid is formed, which contains the hyposulphite, and one of the higher sulphides of the metal; 6 atoms of caustic potash and 12 of sulphur would thus furnish 1 atom of hyposulphite and 2 of persulphide of potassium;  $6KHO + 6S_2 = K_2S_3H_2O_4 + 2K_2S_5 + 2H_2O$ .

(564) POTASSIC CHLORIDE, or *Chloride of potassium* ( $KCl = 74.6$ ); *Sp.Gr.* 1.994: *Comp. in 100 parts*; K, 52.35; Cl, 47.65.—This salt is extracted in considerable quantity from *kelp*, the ashes of burnt sea-weed, and is used largely as a source of the potassic salt required in the manufacture of alum. It may be prepared pure by directly neutralizing either the acid or the normal potassic carbonate with hydrochloric acid, and evaporating. It crystallizes in cubes, and is very readily soluble in cold water, which takes up about a third of its weight, attended with great depression of temperature. It is remarkable that this salt possesses the property of absorbing the vapours of sulphuric anhydride, forming a hard translucent mass ( $KCl, SO_3$ ), which is instantly decomposed by water. With chromic acid it forms a corresponding compound ( $KCl, CrO_3$ ), which is also decomposed by water: it is obtained in

needles when a solution of potassic dichromate in hydrochloric acid is allowed to crystallize.

According to Bunsen, a blue subchloride of potassium also exists.

A native compound of chloride of potassium and magnesium has recently been discovered in a bed of clay in the neighbourhood of Stassfurt, near Magdeburg, where it is immediately above a bed of rock-salt 100 feet or 30 metres in thickness. This is precisely the position which it would occupy, supposing the deposit to have been formed by the gradual drying up of an inland sea, where the common salt would crystallize out first, and the salts of magnesium and potassium afterwards. This bed of clay contains the sulphates and chlorides of potassium, of sodium, and of magnesium, and the upper part of the deposit consists chiefly of a hydrated double chloride of magnesium and potassium, ( $\text{KCl}$ ,  $\text{MgCl}_2, 6\text{H}_2\text{O}$ ), which has received the name of *carnallite*, from its pink colour, resembling rock-salt in appearance, but with a more pearly lustre, and extremely deliquescent. It is now extensively worked for the sake of the potassic chloride, which amounts to nearly one-fourth of its weight.

(565) *Potassic bromide*, or *Bromide of potassium* ( $\text{KBr} = 119.1$ ); *Sp. Gr.* 2.672; *Comp. in 100 parts*, K, 32.83; Br, 67.17.—This is a very soluble salt, which crystallizes in cubes. It may be obtained by adding bromine to a solution of caustic potash until the liquid acquires a slight permanent yellow colour: potassic bromide and bromate are formed. Löwig dissolves the mixed salts in water, decomposes the bromate by a current of sulphuretted hydrogen, warms gently to expel the excess of the gas, filters from the deposited sulphur, and evaporates till the solution crystallizes;  $2\text{KBrO}_3 + 6\text{H}_2\text{S} = 2\text{KBr} + 6\text{H}_2\text{O} + 3\text{S}_2$ .

(566) *POTASSIC IODIDE*, or *Iodide of potassium* ( $\text{KI} = 166.1$ ); *Sp. Gr.* 3.056; *Comp. in 100 parts*, I, 76.44; K, 23.56.—This valuable medicine may be procured in several ways. A simple method consists in adding iodine to a solution of caustic potash gently warmed, until the solution begins to assume a brown tint. Iodide and iodate of potassium are formed;  $3\text{I}_2 + 6\text{KHO} = 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O}$ . By gentle ignition of the residue obtained on evaporation, the iodate is decomposed, and the remaining iodide fuses. The salt must not be strongly heated, as potassic iodide is volatilized by a red heat. A better plan is to digest 2 parts of iodine and 1 part of iron, in a stoppered vessel, with 10 parts of water, the iron being purposely added in excess; under these circumstances ferrous iodide is formed by the direct union of the

metal with the iodine: the solution is decanted, and a quantity of iodine equal to one-third of that which it already contains is added. The liquid is then boiled, and a solution of potassic carbonate is added in small quantities so long as effervescence is produced and a precipitate occurs;  $\text{Fe}_3 + 4\text{I}_2 + 4\text{K}_2\text{CO}_3 = 8\text{KI} + \text{Fe}_3\text{O}_4 + 4\text{CO}_2$ ; the solution is next filtered from the dense magnetic oxide of iron, and on evaporation it yields crystals of potassic iodide.

Potassic iodide crystallizes in anhydrous cubes, which in a dry air are not deliquescent. It is very soluble in water, and to a smaller extent in alcohol; it has a cooling, bitterish taste. Its solution has the property of dissolving an additional equivalent of iodine, with which it forms a deep brown liquid.

Potassic iodide, if pure, should be completely soluble in six times its weight of alcohol (sp. gr. 0.83); it should not effervesce when moistened with hydrochloric acid (carbonate would be indicated by effervescence), and it should not turn brown by the action of the acid; if potassic iodate were mixed with it, free iodine would be shown by the brown colour developed on adding the acid. If the solution of the iodide be mixed with strong nitric acid an immediate separation of iodine occurs;  $2\text{KI} + 4\text{HNO}_3 = 2\text{KNO}_3 + 2\text{H}_2\text{O} + 2\text{NO}_2 + \text{I}_2$ . A mixture of potassic dichromate and sulphuric acid gives a similar result;  $\text{K}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{SO}_4 + 6\text{KI} = \text{Cr}_2\text{SO}_4 + 4\text{K}_2\text{SO}_4 + 7\text{H}_2\text{O} + 3\text{I}_2$ .

(567) POTASSIC FLUORIDE, or *Fluoride of potassium* ( $\text{KF} = 58.1$ ; *Sp. Gr.* 2.454) is a very deliquescent salt obtained by neutralizing hydrofluoric acid with a solution of caustic potash. Its solution has an alkaline reaction and corrodes glass.

(568) POTASSIC SILICOFLUORIDE ( $2\text{KF}, \text{SiF}_4 = 220.3$ ).—This salt is one of the most insoluble compounds of potassium; it falls as a transparent gelatinous precipitate whenever hydrosilicofluoric acid is added to a salt of potassium; it dries to a white earthy-looking powder. Advantage is occasionally taken of its insolubility to separate potassium from some of its salts: in this way chloric acid is sometimes prepared from potassic chlorate.

(569) POTASSIC SULPHATE, or *Sulphate of potassium* ( $\text{K}_2\text{SO}_4 = 174.3$ ); *Sp. Gr.* 2.64; *Comp. in 100 parts*,  $\text{K}_2\text{O}$ , 54.02;  $\text{SO}_3$ , 45.98.—This salt crystallizes either in anhydrous six-sided prisms, terminating in six-sided pyramids, or in four-sided oblique rhombic prisms; it requires about 16 parts of cold water for solution. The crystals decrepitate strongly when heated. Potassic sulphate forms a series of double salts with sulphates of the metals isomorphous with magnesium, and another class of salts (the varieties of alum) with the sulphates of the metals isomorphous with aluminum. Jacquelin finds that if normal potassic sulphate be dissolved in nitric acid, a little nitre and hydro-potassic sul-

phate ( $\text{KHSO}_4$ ) are formed, whilst a salt consisting of ( $\text{HNO}_3$ ,  $\text{K}_2\text{SO}_4$ ) crystallizes in oblique prisms. An analogous compound may be formed with phosphoric acid ( $\text{H}_3\text{PO}_4$ ,  $\text{K}_2\text{SO}_4$ ).

**HYDROPOTASSIC SULPHATE**, *Acid sulphate*, or *Bisulphate of potassium*: ( $\text{KHSO}_4 = 136.1$ ); *Sp. Gr.* 2.475.—This salt is formed on a large scale as a residuary product in the preparation of nitric acid from potassic nitrate. It crystallizes from a strongly acid solution in rhomboidal tables, which fuse at a heat below redness, and by prolonged ignition lose half their acid; they are very soluble in water and have a sour bitterish taste. If redissolved in water, the normal sulphate crystallizes first, and afterwards, when the liquid has become strongly acid, the bisulphate is deposited. This salt is sometimes used as a flux in cases where the action of an acid is required at a high temperature upon salts or metallic oxides with which it may be fused. The bisulphate occasionally crystallizes in anhydrous needles,  $\text{K}_2\text{SO}_4\text{SO}_3$ .

(570) **POTASSIC NITRATE**, or *Nitrate of potassium* ( $\text{KNO}_3$ ,  $= 101.1$ ); *Sp. Gr.* 2.070; *Comp. in 100 parts*,  $\text{K}_2\text{O}$ , 46.54;  $\text{N}_2\text{O}_5$ , 53.46.—*Saltpetre*, or *Nitre* as this salt is frequently termed, is one of the most important and valuable salts of potassium. The principal supply of nitre is derived from various districts in the East Indies, where it occurs sometimes as an efflorescence upon the soil, at other times disseminated through the superficial stratum itself. It appears to be formed in the moist portions of the soil, at some little distance below the surface, towards which it is raised by capillary action. The nitre is obtained by lixiviating the soil, and allowing the solution to crystallize. The earth which furnishes it consists principally of loose porous calcic carbonate, mixed with decomposing felspar, and it always contains more or less of organic matters. In temperate climates, either nitrites or nitrates are almost always found in the shallow well-waters of towns, owing to the oxidation of nitrogen contained in the animal *æbris* during their infiltration through the soil. Notwithstanding the numerous investigations of which it has been the subject, including in later times those of J. Davy, of Kuhlmann, of Schönbein, and others, the process of nitrification is still very imperfectly understood. The artificial formation of nitre has, however, been practised with considerable success in various countries of Europe, which furnish annually a large amount of the salt. In Sweden this supply of nitre is considered of such importance that each landed proprietor is obliged to pay a certain tax in raw nitre, the quantity required being proportioned to the value of the estate.

Where animal matters are present in abundance, the formation of nitric acid is chiefly due to the gradual oxidation of ammonia developed in the process of putrefaction. The free access of air and the presence of a certain amount of moisture is necessary; the oxidation is also materially favoured by an excess of an alkaline or earthy carbonate, or of some basic substance which can combine with the acid at the moment of its generation. Ozone appears to have the power of combining directly with nitrogen; it may possibly, as Schönbein conjectures, be concerned in the natural production of nitric acid, and indeed it is not improbable that nitrification is, in favourable cases, due to the slow combination of atmospheric nitrogen and oxygen. The process of nitrification becomes arrested if the temperature be allowed to fall much below  $59^{\circ}$  ( $15^{\circ}$  C.).

*Nitre Plantations.*—The method adopted for the artificial production of nitre consists in placing animal matters, mingled with ashes and lime rubbish, in loosely aggregated heaps, exposed to the air, but sheltered from rain. These heaps are watered from time to time with urine or stable runnings, the heap being kept damp, but not wet; at suitable intervals the earth is lixiviated, and the salt crystallized. Three years usually elapse before the nitre bed is washed: after this interval a cubic foot of the *débris* should yield between 4 and 5 ounces of nitre, or a cubic metre, about 4 kilos. As there is always a considerable quantity of calcic and magnesian nitrates present, which will not crystallize, potassic carbonate, in the shape of wood ashes, is added so long as any precipitate occurs. By this means the calcic nitrate is decomposed, and the insoluble calcic carbonate separated;  $K_2CO_3 + Ca_2NO_3 = CaCO_3 + 2KNO_3$ . The clear liquor is then evaporated and crystallized. It is found by the saltpetre-boiler that the earth in which nitre has once been formed furnishes fresh nitre more readily than on the first occasion. Care is taken that the *nitre plantations*, as they are termed, shall rest upon an impervious flooring of clay, so that the liquid which drains away from them may be collected and preserved.

In Prussia, by a more methodical treatment, a cubic metre of the earth yields about 20 kilos. of nitre. The heaps are so constructed as to form a terrace of steps, exposing the back in the form of an upright wall to the prevailing wind; the watering is thus facilitated, while the evaporation proceeds with rapidity upon the exposed side, where, from capillary action, the nitre chiefly accumulates: from time to time a layer of earth is removed from this wall for lixiviation, and the washed earth, mixed with a fresh

portion of animal matter, is returned systematically to the other side of the heap. The washing of the earth charged with saltpetre is conducted in a systematic manner (589), so as to avoid using a larger quantity of water than is actually needed to dissolve the saltpetre.

Besides the natural and artificial sources of nitre just described, this salt occurs also in solution in the sap of certain plants, among which the sunflower, the tobacco plant, and common borage may be enumerated.

*Properties.*—Nitre usually crystallizes in long six-sided striated prisms, terminated by dihedral summits; but it is a dimorphous salt, and is occasionally obtained by spontaneous evaporation of small drops of its solution in microscopic rhombohedra, isomorphous with those of sodic nitrate: it is soluble in  $3\frac{1}{2}$  times its weight of cold water, and in about a third of its weight of boiling water; it is insoluble in alcohol: its taste is cooling and saline. If paper be dipped in a solution of nitre and dried, it forms what is well known as *touch-paper*, which, when once kindled, steadily smoulders away till consumed, and hence it is largely employed in firing trains of powder, fireworks, &c. Nitre fuses easily without decomposition at a temperature of  $642^{\circ}\cdot 2$  ( $339^{\circ}$  C.), and when cast into moulds, solidifies to a white, fibrous, translucent, radiated mass, known as *sal prunelle*. When heated to redness, part of its oxygen is expelled, and a deliquescent mass of potassic nitrite is formed. By a still stronger heat the nitrite is decomposed, nitrogen mixed with oxygen escapes, and a mixture of potash and potassic peroxide remains.

Owing to the facility with which nitre parts with oxygen, it is a powerful oxidating agent, and is in frequent demand in the laboratory for this purpose: when thrown upon glowing coals it produces a brisk scintillation. If nitre be intimately mixed with any metallic sulphide in fine powder, such as antimonious sulphide, and thrown, in small quantities at a time, into a red-hot crucible, the sulphur burns with a brisk *deflagration*, or rapid combustion, at the expense of the oxygen of the nitre, and with a portion of its potassium, forms potassic sulphate, whilst the metal at the same time becomes oxidized to the maximum. In the case of antimony, the oxide produced possesses acid characters, and it also enters into combination with the potassium. Baumé's quick flux consists of a mixture of 3 parts of nitre, 1 part of sulphur, and 1 of sawdust; the heat given out during its combustion is so great, that if a small silver coin be put into a mass of the mixture which will go into a walnut-shell, and it be kindled, the

coin will be melted. Advantage is frequently taken of the oxidizing action of nitre in order to convert small quantities of sulphur in bodies of organic origin into sulphuric acid, for the purpose of estimating the proportion of sulphur which they contain. The quantity of sulphuric acid thus produced, admits of easy and accurate determination in the form of baric sulphate.

(571) *Refining of Saltpetre.*—The impurities of most frequent occurrence in nitre are potassic and sodic sulphates and chlorides, and calcic and magnesian nitrates: after it has been fused, unless the heat has been cautiously regulated, a little potassic nitrite is liable to be formed: in the latter case a fragment of the salt, when moistened with solution of cupric sulphate, becomes of a bright green colour. Nitre may be quickly deprived of chlorine by moistening the powdered salt with pure nitric acid and gently heating it, until a portion of it, when dissolved in water, gives no precipitate with argentic nitrate. Nitre, when pure, is not deliquescent, and its solution gives no precipitate with solutions of baric chloride, of argentic nitrate, or of potassic carbonate.

In the refining of nitre, advantage is taken of the circumstance that whilst the solubility of nitre increases rapidly as the temperature rises, that of sodic chloride is scarcely affected by it. It was formerly the practice to purify the salt by three successive crystallizations; but the same object is now effected by a single operation, in the following manner:—In a deep copper boiler, 600 litres, or about 100 gallons, of water is placed, and twice its weight of crude nitre is added: this salt gradually becomes dissolved, and fresh nitre is added, until, when the water has attained the boiling-point, a quantity of nitre has been added equal to three times the weight of the water employed;\* when the liquid has been rendered clear by a few minutes' ebullition, it is strained through bag filters, and allowed to run into the crystallizing pan.

The crystallization is effected in a shallow vessel, the bottom of which is formed by two inclined planes which meet in the middle. In this vessel the solution is kept in continual agitation, in order to prevent the formation of large crystals: such crystals would mechanically retain the mother-liquor, from which they could not be subsequently freed without recrystallization. The sodic chloride, being nearly as soluble in cold water as in hot, remains almost entirely in the solution, whilst the saltpetre is deposited in extremely small crystals, technically termed *saltpetre flour*; these are allowed to drain, and are then removed to tanks provided with false perforated bottoms, where they are deprived of the mother-liquor with which they are saturated. For this purpose, the tanks are completely filled with the crystals, and upon them is poured a solution of saltpetre saturated in the cold; this liquid dissolves the chlorides, but leaves the pure nitre undissolved.

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\* The quantity of sodic chloride in *grough* or crude East Indian nitre is generally small; but in the artificial nitre obtained from the 'beds' it often rises to a large amount: in such a case the liquid is skimmed from time to time, and the sodic chloride, a large proportion of which remains undissolved, is removed by means of perforated ladles; as soon as nitre equal to about 5 times the weight of the water has been added, the solution is diluted with two-thirds the quantity of water at first employed, after which, if the liquid be strongly coloured, 1 kilogramme (about 2½ lbs.) of glue, dissolved in hot water, is added, and thoroughly incorporated by briskly stirring; the coagulum which is formed rises in a scum to the surface, collecting the greater part of the organic impurities derived from the nitre heap; this is carefully removed, and the operation is afterwards continued as above described.

In the course of a few hours, the liquid is drawn off, and the tanks are then filled up with pure water; this becomes charged with nitre containing traces of chlorides, whilst the undissolved salt is almost chemically pure: the solution of nitre thus obtained serves to wash a fresh portion of the crystals; the refined saltpetre is then dried, and is fit for use.

(572) *Gunpowder*.—The principal consumption of nitre is in the manufacture of gunpowder, which consists of an intimate mechanical mixture of nitre, sulphur, and charcoal, in proportions approaching to 1 atom of sulphur, 2 of nitre, and 3 of charcoal :—

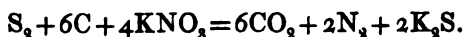
Nitre	...	$2\text{KNO}_3$	=	202	...	In 100 parts. 74·8
Sulphur	...	S	=	32	...	11·9
Charcoal	...	3C	=	36	...	13·3
				<hr/>		<hr/>
				270		100·0

The proportions used vary a little in different countries, as will be seen from the following table :—

*Composition of Gunpowder in 100 parts.*

	English and Austrian.	Prussian.	Swedish.	Chinese.	French.		
Nitre ...	75	75·0	75	75·7	75·0	76·9	62
Sulphur ...	10	11·5	9	9·9	12·5	9·6	20
Charcoal ...	15	13·5	16	14·4	12·5	13·5	18
	Musket.	Musket.	Musket.		Musket.	Sporting.	Blasting.

An excess of sulphur is carefully avoided, on account of its injurious action upon the metal of the gun. The great explosive power of gunpowder is due to the sudden development of a large volume of gaseous bodies, consisting chiefly of nitrogen and carbonic anhydride, which, at the ordinary temperature of the air, would occupy a space equal to about 300 times the bulk of the powder used; but from the intense heat developed at the moment of the explosion, the dilatation amounts to at least 1500 times the volume of the gunpowder employed. Supposing the mixture to be made in the proportion of 1 atom of sulphur, 2 atoms of nitre, and 3 of carbon, the reaction is often approximatively represented thus :—



The actual results, however, cannot readily be represented by any simple formula, and the solid residue, instead of consisting chiefly of potassic disulphide, contains but a small quantity of



this substance, whilst potassic sulphate and carbonate are found in abundance: they become volatilized by the heat of the explosion, and constitute the white smoke observed when gunpowder is fired.\*

Much care is requisite in the selection of the materials for the manufacture of gunpowder. The charcoal must be burned thoroughly, but not at too high a temperature: that from the willow, alder, or dogwood is preferred for the purpose, dogwood charcoal being employed only in making rifle powder. The charcoal always contains a notable proportion of hydrogen and oxygen. In the Government works at Waltham Abbey, sulphur is never used in the state of flowers of sulphur; in this condition it is preferred for fireworks; but distilled sulphur, reduced to a fine meal by grinding, is always used for gunpowder. The flowers of sulphur always contain sulphurous acid, which becomes speedily converted into sulphuric acid and attracts moisture. Nitre of the purest quality is alone employed. These three materials having been separately ground and sifted, are mixed in powder in the proper proportions, and are intimately blended in a revolving drum; they are then made into a stiff paste with water, and ground for some hours under edge-stones in the *incorporating-mill*; the slightly coherent mass thus procured is broken up, and spread, in layers of about an inch in thickness, between plates of gun-metal; it is then subjected to the action of a hydraulic press which exerts a force of 70 tons upon the square foot: a hard sonorous mass, termed *press cake*, is thus obtained: these masses, while still damp, are broken into small fragments, or *granulated*, by submitting them to the action of toothed rollers in a machine constructed for the purpose. The grains are next sorted by means of sieves into different sizes, after which they are thoroughly dried in closets heated by steam, and, finally, are *glazed*, or polished by placing them in barrels caused to revolve about 30 times in a minute. Mining powder is often glazed by adding powdered graphite in the polishing barrels; this operation retards the rate of ignition, and diminishes the hygroscopic character of the powder. A cubic foot of good English cannon powder weighs about 58 lb.; if below 55 lb., it is considered unfit for use. The heavier the powder the greater is its explosive power. Two ounces of the best English powder, when introduced into a mortar of 8 inches diameter, set at an angle of  $45^\circ$ , should throw a 68 lb. shot from 260 to 280 feet, on level ground.

Good gunpowder burns rapidly in the open air, leaving little residue, not blackening or kindling paper upon which it is fired. It has been found that a powerful concussion of powder between two pieces of iron will frequently kindle it, and if the powder be

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\* In burning gunpowder in a copper tube with the view of collecting the gases over mercury, Chevreul found a small proportion of nitric oxide, of carbonic oxide, and of carburetted hydrogen, with a little sulphuretted hydrogen, mixed with the nitrogen and carbonic anhydride. Bunsen, and Linck, obtained results somewhat different, but the temperature, and consequently also the results of the combustion procured by this regulated action, are different from those attending the firing of ordnance. Karolyi, however (*Phil. Mag.* Oct. 1863), has succeeded in analysing the gases of gunpowder which had been fired in conditions closely resembling those which occur in artillery practice. For this purpose he enclosed a charge of powder in an iron cylinder of such strength that it just burst when the powder was fired by means of the electric spark. This charged cylinder was suspended in a hollow spherical bomb, from which the air was

placed upon lead, or even upon a board, it may be exploded by the blow of a leaden bullet fired at it. The temperature at which it takes fire is about  $482^{\circ}$  ( $250^{\circ}$  C.)

exhausted before firing. After the explosion had been produced, the gases and the solid residue of the powder were submitted to analysis. The results obtained were the following:—

1. *Composition of the Powder used.*

			Ordnance powder.		Small-arms powder.
Nitre	...	...	73.78		77.15
Sulphur	...	...	12.80		8.63
Charcoal	{ Carbon	...	10.88	13.39	11.78
	{ Hydrogen	...	0.38		0.42
	{ Oxygen	...	1.82		1.79
	{ Ash	...	0.31		0.28
			99.97		100.05

2. *Products of Combustion by weight.*

Gaseous	{ Nitrogen	...	9.77	30.58	10.06	34.18
	{ Carbonic anhydride	...	17.39		21.79	
	{ Carbonic oxide	...	2.64		1.47	
	{ Hydrogen	...	0.11		0.14	
	{ Sulph. hydrogen	...	0.27		0.23	
	{ Marsh gas	...	0.40		0.49	
Solid	{ Ammonic sesquicarb.	...	2.68	69.25	2.66	65.14
	{ Potassic sulphate	...	36.95		36.17	
	{ „ carbonate	...	19.40		20.78	
	{ „ hyposulphite	...	2.85		1.77	
	{ „ sulphide	...	0.11		0.00	
	{ Charcoal	...	2.57		2.60	
	{ Sulphur	...	4.69		1.16	
	{ Loss	...	0.17		0.68	
			100.00		100.00	

3. *Products of Combustion by volume in 100 of Gas.*

Nitrogen	...	...	37.58	100.0	35.33	100.0
Carbonic anhydride	...	...	42.74		48.90	
Carbonic oxide	...	...	10.19		5.18	
Hydrogen	...	...	5.93		6.90	
Sulphuretted hydrogen	...	...	0.86		0.67	
Marsh gas	...	...	2.70		3.02	

These gases contained a sufficient amount of carbonic oxide, and of hydrogen and its compounds, to take fire on the application of a lighted match. The formation of ammonic sesquicarbonate and of potassic carbonate in such large proportion is remarkable. The results obtained by the analysis of sporting powder by Bunsen and Schischkoff (*Poggend. Annal.* cii. 321) do not materially differ from those quoted above; but are slightly modified by the excess of nitre used in the preparation of this kind of powder.

The object of granulating the powder, independently of the diminution of its tendency to absorb moisture, is to favour the rapidity of inflammation, by leaving interstices through which the flame is enabled to penetrate and envelope each grain. The ignition of the whole charge does not take place simultaneously throughout, nor is it desirable that it should do so, otherwise sufficient time would not be given to allow the ball to receive the full advantage of the expansive force of the air generated; too rapid an action would be expended upon the barrel of the gun itself, and effects would be produced like those due to fulminating mercury; where a prolonged heaving force is required, as in blasting for mining operations, the action of the powder is still further retarded by mixing it with sawdust; the powder employed for this purpose usually contains 65 parts of nitre, 20 of sulphur, and 15 of charcoal. In the formation of the fusee, the quick and slow match, and certain kinds of fireworks, gunpowder is mingled with combustibles in various proportions.

The analysis of gunpowder is easily effected: 100 grains of the powder for examination are dried over sulphuric acid *in vacuo*; the loss indicates the amount of moisture. The residue is digested in water, and washed: the solution, when evaporated in a counterpoised capsule, and weighed, furnishes the amount of nitre and other salts. Baric nitrate, when added to a solution of these salts, acidulated with nitric acid, will yield the sulphuric acid in the form of baric sulphate; and argentic nitrate, when added to the liquid filtered from the baric sulphate, will give the data for ascertaining the amount of chlorine from the precipitated argentic chloride. The charcoal and sulphur are contained in the portion which does not dissolve in water; they may be separated by means of carbonic disulphide or by the use of benzol at a boiling temperature, which dissolves out the sulphur, and leaves it in the crystalline form by spontaneous evaporation, whilst the charcoal is left undissolved and may be weighed.

A mixture of 3 parts of nitre, 2 of potassic carbonate, and 1 part of sulphur, produces a substance known as *pulvis fulminans*, which when heated on an iron shovel until fusion takes place, explodes suddenly with a very loud report.

(573) POTASSIC NITRITE, or *Nitrite of potassium* ( $\text{KNO}_2$ ), is a white anhydrous, deliquescent salt, which may be obtained in crystals. It may be procured by decomposing nitre by fusion at a red heat, dissolving the residue in water, and allowing the nitre to crystallize out of the deliquescent nitrite, which may be obtained by evaporating the solution to dryness.

(574) POTASSIC CHLORATE, or *Chlorate of potassium* ( $\text{KClO}_3$ , =122.6); *Sp. Gr.* 2.326; *Comp. in 100 parts*,  $\text{K}_2\text{O}$ , 38.36, and  $\text{Cl}_2\text{O}_6$ , 61.64.—One mode of preparing this salt has already been explained (382). It may be more economically obtained by converting milk of lime into a mixture of calcic chlorate and chloride by transmitting chlorine gas in excess; to a concentrated solution of the mixed salts, potassic chloride is then added in the

proportion of 74.5 parts of the chloride to 168 parts of the caustic lime originally employed. The calcic chlorate and potassic chloride decompose each other, and potassic chlorate and calcic chloride are formed ( $\text{Ca}_2\text{ClO}_3 + 2\text{KCl} = 2\text{KClO}_3 + \text{CaCl}_2$ ); boiling water dissolves both the potassic chlorate and the calcic chloride. The two salts are easily separated by crystallization, as the chlorate requires 16 parts of cold water for solution, and the chloride is soluble to almost any extent. From this mixture the crude chlorate is deposited in 6-sided prisms, which, on being redissolved in water, are crystallized in anhydrous rhomboidal pearly tables; it has a cooling taste, somewhat analogous to that of nitre: 100 parts of boiling water dissolve 61.5 of the salt. When heated to between  $698^\circ$  and  $806^\circ$  ( $370^\circ$  and  $430^\circ$  C.), the salt melts, and at a higher temperature is decomposed, furnishing oxygen gas of great purity, and leaving potassic chloride as a fixed residue behind. When heated to redness, 100 parts of the salt leave 60.79 parts of potassic chloride, and 39.21 of oxygen are evolved. The chlorate is a more powerful oxidizing agent than nitre; and if combustible substances, such as sulphur or phosphorus, be rubbed with it forcibly, the combination of the combustible with oxygen ensues, accompanied by detonation. Potassic chlorate is principally consumed in the manufacture of lucifer matches, and as an oxidizing agent in certain operations of the calico-printer. When added to a solution acidulated with hydrochloric acid, it is often used in the laboratory as an oxidizing agent.

The friction tubes employed for firing cannon are charged with a mixture of 2 parts of potassic chlorate, 2 of antimonious sulphide, and 1 part of powdered glass. A mixture known under the name of *white gunpowder*, consisting of 2 parts of potassic chlorate, 1 part of dried potassic ferrocyanide, and 1 of sugar, has sometimes been manufactured for blasting purposes; but its preparation is attended with very great danger, owing to the facility with which it explodes by friction, a circumstance which has caused several fatal accidents.

(575) POTASSIC PERCHLORATE, or *Perchlorate of potassium* ( $\text{KClO}_4$ ,  $\approx 138.6$ ); *Comp. in 100 parts*,  $\text{K}_2\text{O}$ , 33.93;  $\text{Cl}_2\text{O}_7$ , 66.07.—This salt crystallizes in anhydrous prismatic needles, which are very sparingly soluble in cold water; its principal properties and the mode of preparing it have been already described (383). When heated to redness it gives off 46.11 per cent. of oxygen, leaving 53.89 of potassic chloride.

(576) POTASSIC CARBONATE, or *Carbonate of potassium* ( $\text{K}_2\text{CO}_3$ ,  $\approx 138.3$ ); *Sp. Gr.* 2.267; *Comp. in 100 parts*,  $\text{K}_2\text{O}$ , 68.11;  $\text{CO}_2$ , 31.89.—This important salt is obtained in large quantities for commercial purposes by lixiviating wood ashes, and evaporating the solution until it crystallizes; the mother-liquor, when it cools, is poured off from the crystallized salts, as it retains the more soluble potassic carbonate, and when evaporated to dryness,

affords the *potashes* of commerce, and these, when calcined, yield the impure carbonate known as *pearlash*. Different plants, when burned, furnish varying quantities of the alkali, which they extract from the soil: the leaves and young shoots, where the vital action is the most vigorous, are the parts which furnish the greatest quantity of alkali. Herbaceous plants, therefore, generally furnish more than shrubs, and shrubs more than an equal weight of timber. It appears from the experiments of Violette that the variation in the quantity of crude ash obtained from different parts of the same tree is extremely great. Taking, for instance, the quantity of ash found in the heart-wood as the unit of comparison, the proportion in other parts was as follows:—

Heart-wood	...	1	Bark of branches...	11
Root bark	...	5	Root fibres	15
Bark of trunk	...	9	Leaves	25

and it is stated by Chevandier (*Ann. de Chimie*, III. x. 129) that the quantity of ash varied as follows for 100 parts of different portions of the wood of the undermentioned trees after drying at 284° (140° C.);—

		Solid Stem.	Arms.	Small branches.
Beech	...	0.91	2.15	1.29
Oak	...	2.43	2.03	1.68
Birch	...	0.71	1.03	0.60

As an average it may be stated that 1000 parts of timber yield from 2 to 4 parts of pearlash.

In the wine-producing countries, a considerable quantity of pearlash of good quality is furnished by burning the refuse yeast after the fermentation is complete. The yeast, for this purpose, is pressed, dried in the sun, and burned in shallow enclosures: this dry yeast furnishes nearly 10 per cent. of its weight of the carbonate. Potassium does not exist in plants in the form of carbonate; it occurs in them in union with the oxions of different organic acids: these organic acids are destroyed by the action of the heat during incineration. Such acids always contain more carbon than is sufficient, when oxidized by the air, to form the amount of carbon requisite to neutralize the potassium; and the potassic carbonate thus produced remains behind, as it is not decomposed by a red heat. In the ashes of plants various other saline substances are likewise present, but those which are soluble consist, in addition to the carbonate, principally of potassic sulphate and chloride; these alkaline salts usually amounting to from 10 to 20 per cent. of the entire quantity of ash.

A purer carbonate is obtained for chemical purposes by defla-

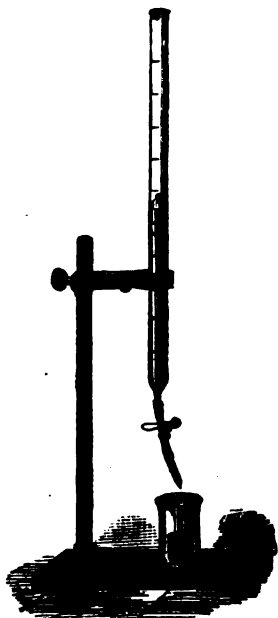
grating a mixture of purified cream of tartar with an equal quantity of pure nitre. The mass is thrown, in small portions at a time, into a red-hot crucible: in this operation the nitre yields oxygen to the vegetable acid, converting its carbon into carbonic acid, which enters into combination with the alkali both of the tartar and of the nitre, since the two acids undergo mutual decomposition: the carbonate is extracted from the dry mass by lixiviation.

Potassic carbonate is a deliquescent salt, which is with difficulty obtained in oblique rhombic octohedral crystals ( $K_2CO_3 \cdot 2H_2O$ ). Its reaction upon test-paper is strongly alkaline; it has an acid, alkaline taste. Its solutions have a peculiar lixivial smell: 100 parts of water at  $59^\circ$  ( $15^\circ$  C.) dissolve 90 of the carbonate; and at the boiling-point take up 205 parts, or rather more than twice their weight, of the salt. Alcohol does not dissolve it. Potassic carbonate fuses by exposure to a red heat, and at a very high temperature is partially volatilized; at a red heat it is decomposed by silica, carbonic anhydride being expelled with effervescence, whilst the silica, uniting with the alkali, forms with it a true silicate, the basis of one of the varieties of glass. Advantage is taken of this property, in the analysis of mineral substances which contain a large quantity of silica, and which are not easily decomposed by the action of acids. For this purpose the mineral to be analysed is reduced to an extremely fine powder by careful levigation; a portion of this powder is accurately weighed, and then intimately mixed with about 3 times its weight of potassic carbonate (or, still better, with thrice its weight of a mixture of  $5\frac{1}{2}$  parts of dried sodic carbonate and 7 of potassic carbonate); the whole is introduced into a platinum crucible, and exposed to a bright red heat for an hour. The mass enters into fusion, carbonic anhydride escapes with effervescence, and a silicate of potassium is formed; by which means all the bases of the mineral, which before were combined with the silica, are set at liberty. Upon now treating the mass with diluted hydrochloric acid, the silicate is decomposed, the earths and metallic oxides are dissolved, and the silica is partially dissolved and partially separated in the hydrated form. In order to decompose the hydrate of silica, the solution is evaporated to dryness, moistened with hydrochloric acid, and again treated with water; the whole is now placed upon a filter, and the silica, after being well washed, remains behind in a state of purity. The analysis of the filtered liquid is then finished according to the ordinary method adopted for substances directly soluble in acids.

Potassic carbonate is largely consumed in the arts, as for example, in the manufacture of soap and of glass, and for preparing caustic potash and other compounds of potash. It also furnishes the chemist with one of his most indispensable reagents.

(577) *Alkalimetry*.—Since the quantity of alkaline carbonate, technically known as *alkali*, is liable to great variations in different samples of the ash,—and since the commercial value of pearlash depends upon the amount of carbonate which it contains, a rapid and sufficiently accurate method of analysis of this salt becomes a desideratum. In order to effect this object, the process termed *alkalimetry* has been invented. In principle it depends upon the determination of the number of divisions of a diluted acid, of definite strength, which 100 grains of the different samples of ash are capable of neutralizing; the neutralization being estimated by the action of the solution upon blue litmus.

The acid solution which is to be employed is measured from a burette or *alkalimeter*, Mohr's form of which is shown in fig. 339. It consists of a glass tube, with an internal diameter of about five-eighths of an inch, and is sufficiently tall to contain rather more than 1000 grains of distilled water. A little water, say 15 or 20 grains, is introduced into the tube, and the level of its surface marked with a line, numbered 100. 1000 grains of water at 60° F. are then added, and the level of its surface again marked off and indicated as 0; the interval is then subdivided into 100 equal parts, each capable of containing 10 grains of water; opposite every tenth division the number corresponding to it is placed, the numbers increasing from above downwards.



If the alkali be dissolved in a beaker, the acid is added in the necessary quantity. By means of the spring clamp *s*, shown nearly at its full size in fig. 340,

the quantity of acid may be regulated with the greatest precision. The spring is arranged so as to pinch the sides of the caoutchouc tube together, and prevent the escape of liquid; but on compressing the studs between the finger and thumb, the pressure of the spring on the caoutchouc is relaxed, to an extent which

may be varied at pleasure; and it can be instantly restored by allowing the spring to exert its natural effect.

FIG. 340.

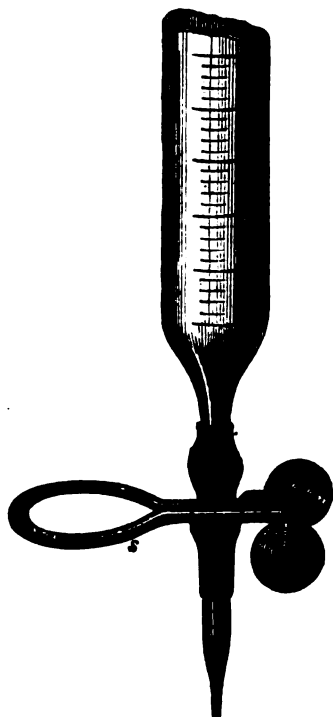


FIG. 341.



Erdmann's float, shown in fig. 341, enables the observer readily to subdivide each division of the burette into tenths; for by reading the level of the liquid at the line, *a*, traced round the float, instead of at the upper curved edge of the liquid, the observation is rendered much more exact.

Various plans have been proposed for preparing the diluted acid; the following will answer the purpose.

The acid preferred is, the sulphuric. If pure acid ( $\text{H}_2\text{SO}_4$ ) be used, the proportion required will be represented by the proportion of the equivalents of the two substances:—

$$\begin{array}{ccccccc}
 1 \text{ at. } \text{K}_2\text{CO}_3 & & 1 \text{ at. } \text{H}_2\text{SO}_4 & & \text{K}_2\text{CO}_3 & & \\
 138 & : & 98 & : : & \text{grains.} & & \\
 & & & & 100 : x (=71.0). & & 
 \end{array}$$

1000 grains would therefore contain 71.0 grains of the acid, and a gallon of the diluted acid (70,000 grs.) would contain 70 times this quantity, or 4970 grs. The commercial acid, however, is never quite pure, and always contains an excess of water, so that



about 5000 grains will be requisite. Having weighed out this amount of oil of vitriol, it is to be added cautiously to a quantity of distilled water, coloured by the addition of about a twentieth of its bulk of tincture of litmus; and the volume of liquid, when cool, is to be made up exactly to one gallon. In order to ascertain whether the strength of this alkalimetric acid be accurately adjusted, a quantity of crystallized bicarbonate of potassium is fused in a platinum crucible in order to convert it into the normal carbonate: the fused mass is poured upon a clean iron plate, and 100 grains of it are quickly weighed, and dissolved in about 3 ounces of water in a small evaporating basin. Diluted acid is now to be introduced into the alkalimeter until it stands at the mark 0: after which the liquid is added to the solution of potassic carbonate, which is to be gently warmed in order to expel the carbonic anhydride as it is liberated; the acid is cautiously added until the litmus is distinctly but permanently reddened. The acid liquid, if properly diluted, ought to contain, in each division, sufficient sulphuric acid to neutralize 1 grain of potassic carbonate, and the entire 100 divisions of the alkalimeter should therefore exactly produce this effect. If more than 100 divisions of the acid be required, the test acid is too weak; if less than 100 divisions, it is too strong.

Suppose that 95 divisions of the acid were sufficient, the alkalimetric acid from which it was prepared must have contained one-twentieth too much acid; every 95 measures of this acid, therefore, must be diluted with 5 measures of water. If, on the other hand, more acid than 100 divisions be required, say 105 be needed, the acid contains one-twentieth too much water; the quantity of alkalimetric acid used in the experiment requires the addition of one-twentieth more of acid than it originally contained. The alkalimetric acid, when duly adjusted, is preserved in bottles which are accurately closed.

Having thus prepared a test acid of the proper strength, 100 grains of the sample of pearlash for trial are dissolved in 3 or 4 ounces of water, filtered if necessary, and then tested in the same manner: the number of divisions of acid consumed will indicate the per-centage of potassic carbonate present in the sample.

A similar method may be employed to determine the quantity of soda present in any sample of soda ash; but as a certain weight of soda neutralizes a proportionately larger amount of acid than an equal weight of potash, a stronger acid must be used in the alkalimeter.

The quantity of acid required to neutralize 100 grains of pure soda,  $\text{Na}_2\text{O}$ , may be calculated in the following manner:—

$$\begin{array}{ccccccc} \text{Na}_2\text{O} & & \text{H}_2\text{SO}_4 & & \text{Na}_2\text{O} & & \\ 1 \text{ st.} & & 1 \text{ st.} & & \text{grains.} & & \\ 62 & : & 98 & : : & 100 & : & x (=158\cdot06). \end{array}$$

1000 grains of the dilute acid must therefore contain 158·06 grains of oil of vitriol, and a gallon seventy times this amount, or 11064·2 grains. In practice, 11200 grains may be taken; and the acid tested by means of pure sodic carbonate, obtained by fusing a little of the pure sodic bicarbonate. The quantity of sodic carbonate required will be such an amount as contains 100 grains of  $\text{Na}_2\text{O}$ ; and this may be ascertained as follows:—

$$\begin{array}{ccccccc} \text{Na}_2\text{O} & & \text{Na}_2\text{CO}_3 & & \text{Na}_2\text{O} & & \text{Na}_2\text{CO}_3 \\ 1 \text{ st.} & & 1 \text{ st.} & & \text{grains.} & & \text{grains.} \\ 62 & : & 106 & : : & 100 & : & x (=170\cdot97). \end{array}$$

or 1000 grains of the diluted acid should exactly saturate 170·97 grains of pure sodic carbonate. Each division of the alkalimetric acid will then correspond to 1 grain of soda, or 1 per cent. of pure soda in 100 grains of any sample of soda ash. If necessary, the test acid must be corrected by adding more acid or more water until the required strength is reached exactly.

In cases where greater accuracy is required, the acid solution, instead of being measured from the burette, is weighed; and for this purpose, the solution is placed in a light flask of the form shown in fig. 342.

In estimating the value of soda ash, which often contains sodic sulphide and hyposulphite, an error might be occasioned by adopting this method; because both the sulphide and the hyposulphite would be decomposed by the sulphuric acid, and would neutralize it, and thus would be reckoned as sodic carbonate.

The presence of caustic alkali in any sample is easily ascertained by the action of the solution upon argentic nitrate: the carbonates of the alkali-metals occasion a white precipitate of argentic carbonate; but if they contain any caustic alkali, a brown precipitate of hydrated argentic oxide is produced. The presence of sulphides in the ash is immediately manifested by the odour of sulphuretted hydrogen which is evolved on neutralizing the solution with an acid; if any sulphide be present, it will blacken the salts of silver, and interfere with their application as a test for caustic potash or soda.

(578) *Alkalimetry; Process of Will and Fresenius.*—The proportion of carbonic anhydride in any sample of alkali is readily ascertained by means of the apparatus employed for the purpose by Will and Fresenius, represented in fig. 343: *b* is a light flask of about 100 cub. centim. capacity, in which 5 grammes of the alkali are placed with about 30 cub.

FIG. 342.



FIG. 343.



cent. of water; *d* is a similar flask, in which about 40 cub. centim. of oil of vitriol is placed. A sound cork is fitted into the neck of each flask, and is pierced with two apertures for the reception of the tubes, *a*, *c*, and *e*, all of which are open at both ends: the tube, *a*, is sufficiently long to dip into the liquid in the flask; *c* is a bent tube, the longer limb of which passes into the acid in the flask, *d*. The outer extremity of *a* is closed during the experiment, by a plug of wax or of soft cement. The apparatus is charged in the manner already described, and is accurately weighed after it has been connected together. A partial vacuum is now made by applying the mouth to the tube, *e*, and exhausting a portion of the air; on ceasing to exhaust, the acid rises in the tube, *c*, and passes over into *b*, to supply the place of the air which has been withdrawn; effervescence is occasioned by the escape of the carbonic anhydride, which passes off through the tube, *c*, and is dried as it bubbles up through the oil of vitriol in the flask, *d*. As soon as the effervescence has ceased, a fresh portion of acid is forced over from *d* into *b* by again partially exhausting the air: and this process is repeated until no further effervescence is occasioned by the fresh acid. The plug of wax is now withdrawn from the tube *a*, and a current of air is drawn through the apparatus by exhausting with the mouth at *e*, and the carbonic anhydride is thus completely displaced. The plug is now replaced in the tube *a*, and the apparatus is weighed a second time. The difference between this weight and that obtained on the first occasion, indicates the amount of carbonic anhydride which has been expelled.

If any sulphide or sulphite of the alkali-metal be present, the error which it might occasion by loss of sulphuretted hydrogen, or of sulphurous anhydride, in the gaseous state, and which would be reckoned as carbonic anhydride, is prevented by mixing an equal weight of potassic chromate with the sample under trial: the chromic acid which is liberated by the subsequent action of the sulphuric acid upon the chromate, imparts oxygen to the sulphuretted hydrogen or sulphurous acid, and converts both into sulphuric acid, which would be retained, and would in no way interfere with the result.

(579) *Hydropotassic carbonate*, *Acid carbonate* or *Bicarbonate of potassium* ( $\text{KHCO}_3 = 100$ ); *Sp. Gr.* 2.052.—By passing a current of carbonic acid through a strong solution of potassic carbonate, crystals of the bicarbonate are deposited in the form of right rhombic prisms; they are permanent in the air, and require about 4 parts of cold water for solution. The solution of the bicarbonate, if exposed to the atmosphere, gradually loses one-fourth of its carbonic acid, forming the so-called sesquicarbonate; and if boiled, the same change occurs much more quickly. The acid carbonate is converted into the normal carbonate when fused by means of heat. Hydropotassic carbonate has no alkaline reaction upon turmeric. It may be employed for procuring the compounds of potassium in great purity, since, if well crystallized, it is almost absolutely pure, and may be obtained in this state with less difficulty than any other salt of potassium. It is consumed medicinally in considerable quantities, for making effervescing draughts by the addition of citric or tartaric acid to its solution in water.

The *Silicates of Potassium* are important compounds in con-

nexion with the manufacture of glass: they will be noticed in treating this subject (594 *et seq.*).

(580) **CHARACTERS OF THE SALTS OF POTASSIUM.**—The salts of potassium, with a colourless acid, are all colourless. They seldom contain any water of crystallization, yet many of them are deliquescent; the carbonate and acetate offer striking instances of this peculiarity, and furnish in this respect a marked contrast to the corresponding salts of sodium. The salts of potassium, when pure, if introduced upon a platinum wire into the *reducing flame of the blowpipe*, communicate to it a violet tint; the presence, however, of a small quantity of a salt of sodium masks this effect, in consequence of the strong yellow flame occasioned in similar circumstances by the compounds of sodium; by means of the spectroscope, however, the potassium is distinctly recognizable, though the sodium salt may be in very large excess. The light emitted by a salt of potassium, in the flame of a Bunsen burner, consists of a feeble continuous spectrum, terminated at one end by a bright line in the red, and at the other by a feebler bright line in the violet (K, fig. 83, page 180, Part I.). Solutions of the salts of potassium yield no precipitate with solutions of the carbonates of the alkali-metals, with potassic ferrocyanide, or with hydro-ammonic sulphide. The presence of potassium in solution is recognized, after the absence of every metal but sodium has been ascertained, by the following characters: if moderately concentrated, a solution of *tartaric acid* in excess causes, upon brisk stirring, a white crystalline precipitate of hydropotassic tartrate ( $\text{KHC}_4\text{H}_4\text{O}_6$ ), which is readily dissolved upon adding an alkali. *Sodic perchlorate*, or *sodic carbazotate* has also sometimes been employed as a test for potassium, since both the perchloric and carbazotic acids form potassium salts of sparing solubility. These compounds, however, are all soluble to a considerable extent in cold water, and unless tolerably strong solutions are employed, they do not immediately subside. With *silicofluoric acid* they yield a transparent gelatinous silicofluoride, which forms a white powder on drying. The most conclusive reaction, however, is produced with *platinic chloride*; upon mixing a strong solution of this salt with a concentrated one of a salt of potassium, a yellow double salt, consisting of  $(2\text{KCl}, \text{PtCl}_2)$  is separated in crystals; it is quite insoluble in alcohol and ether, but is slightly taken up by cold water. It is therefore best for analytical purposes to acidulate the solution suspected to contain potassium

with a little hydrochloric acid, and having added a slight excess of the solution of platinic chloride, to evaporate to dryness over the water-bath, and to wash the residue with alcohol so long as anything is dissolved. This salt when heated to redness is decomposed, the platinum loses its chlorine, and the potassic chloride may be dissolved out of the grey residue with cold water, whilst metallic platinum is left behind: 100 parts of the chloride of platinum and potassium are equivalent to 15.98 of potassium, or to 19.26 of potash, ( $K_2O$ ).

§ II. SODIUM (Natrium): [ $Na=23$ ]. *Sp. Gr.* 0.972;  
*Fusing-pt.*  $207^{\circ}.7$  ( $97^{\circ}.6$  C.).

(581) SODIUM may be obtained from its carbonate by a process analogous to that used in procuring potassium. Deville recommends the employment of the following mixture in the extraction of sodium: dried sodic carbonate, 717 parts; powdered charcoal, 175 parts; finely powdered chalk, 108. These materials are mixed intimately and kneaded into a stiff paste with oil, and calcined in a covered iron pot; the mass is then introduced into an iron retort and distilled, with the precautions described when speaking of potassium; it ought to yield nearly one-third of its weight of sodium: the object of adding the chalk is to prevent the charcoal from separating from the sodic carbonate when this salt fuses. The metal is now prepared in considerable quantities by this method, wrought-iron cylinders with moveable ends being substituted for the mercury bottles used in preparing potassium. The iron cylinders are protected from the fire by an exterior cylinder of clay.

As a reducing agent sodium is but little inferior to potassium in energy, and since its combining number is lower, and the metal is much less expensive, it may generally be substituted for potassium with advantage in such operations.

Sodium has a bluish-white colour; in appearance and properties it much resembles potassium, but is somewhat more volatile; it fuses at a temperature of  $207^{\circ}.7$  ( $97^{\circ}.6$  C.). It burns with a bright yellow flame. When dropped into cold water, it decomposes a portion of it, extricating hydrogen, but the gas does not take fire unless the water be heated previously.

The great storehouse of sodium is common salt, which is met with in nature in extensive deposits; it is also contained in vast quantities in the water of the ocean; the immense quantities of soda consumed in the arts are almost exclusively obtained from chloride of sodium, by a process presently to be described, though

sodium occurs in several minerals, such as albite or sodium-felspar, and cryolite, the double fluoride of sodium and aluminum. Borax or the acid borate of sodium, and trona or the sesquicarbonate, as well as the nitrate, are also native compounds of sodium.

The metal forms two well-known oxides, one of which contains twice as much oxygen as the other:—

Soda ... ..	$\text{Na}_2\text{O} = 62$	Sodium.	74.19	+	Oxygen.	25.81	=	100
Sodic peroxide ...	$\text{Na}_2\text{O}_2 = 78$		58.97	+		41.03	=	100

A blue suboxide appears also to exist.

(582) **SODIC OXIDE**, or *Soda* ( $\text{Na}_2\text{O}=62$ ), forms the base of the important series of salts of sodium. It can be procured in the anhydrous state by burning the metal in dry air or in oxygen gas: it is of a yellowish-white colour, attracts moisture as greedily as the corresponding oxide of potassium, and this water cannot again be expelled from it by heat.

In appearance and properties the *hydrate* or *caustic soda* closely resembles caustic potash; it may be formed from the carbonate by a similar method; its action upon acids, however, is less energetic. According to Filhol the solid hydrate ( $\text{NaHO}$ ) has a sp. gr. of 2.13. (*Comp. in 100 parts*,  $\text{Na}_2\text{O}$ , 77.5;  $\text{H}_2\text{O}$ , 22.5). The following table shows the proportion of anhydrous soda which is contained in solutions of sodic hydrate of different densities:—

*Strength of Solutions of Caustic Soda (Dalton).*

Sp. gr.	$\text{Na}_2\text{O}$ in 100 parts.	Sp. gr.	$\text{Na}_2\text{O}$ in 100 parts.
1.56 ...	41.2	1.32 ...	23.0
1.50 ...	36.8	1.29 ...	19.0
1.47 ...	34.0	1.23 ...	16.0
1.44 ...	31.0	1.18 ...	13.0
1.40 ...	29.0	1.12 ...	9.0
1.36 ...	26.0	1.06 ...	4.7

Caustic soda is extensively used in the manufacture of hard soaps.

Caustic soda is now manufactured on a large scale in the alkali works, which supply it in the form of a solid hydrate containing 60 per cent. of anhydrous soda; for this purpose advantage is taken, as proposed by Mr. Gossage, of the caustic soda present in the solutions of crude soda.

In order to effect this the crude solution obtained from the black-ash vats is evaporated down till it acquires a sp. gr. of 1.5 or 1.6, during which opera-

tion almost all the carbonate, sulphate, and chloride of sodium crystallize out. The solution (technically known as *red liquor*) is of a red colour, owing to the presence of a peculiar soluble compound of sulphide of sodium and sulphide of iron, and is likewise contaminated with ferrocyanide, and occasionally with sulphocyanide of sodium. By forcing air under pressure for several hours through the hot liquid, the iron is precipitated as sesquioxide, and the sulphur compounds are converted into sulphates. The completion of the oxidation is effected by the addition of sodic nitrate. The entire process of oxidation may indeed be more rapidly effected by means of the nitrate. After its addition the evaporation is carried further, until the mass by degrees becomes heated nearly to redness. When the temperature rises to  $311^{\circ}$  ( $155^{\circ}$  C.) large quantities of ammonia are evolved, and subsequently, as the heat becomes much greater, nitrogen escapes abundantly (Pauli). The ammonia is produced partly by the decomposition of the cyanogen compounds, but also in part from the removal of oxygen from water by the sulphides, whilst the hydrogen reduces the nitric acid to the form of ammonia. The fused soda is poured into sheet-iron vessels, in which it solidifies, and is preserved for the market. (*Hofmann's Jury Report, Int. Exhib. 1862, p. 28*).

The *sulphides* of sodium correspond in number with those of potassium, which they closely resemble. They may be prepared by analogous methods.

(583) SODIC CHLORIDE, or *Chloride of sodium* ( $\text{NaCl} = 58.5$ ); *Sp. Gr.* 2.24; *Comp. in 100 parts*, Na, 39.32; Cl, 60.68.—This important and well-known compound, formerly called *muriate of soda*, constitutes common culinary table-salt. It is found native in the solid form, and it exists in solution in sea water in a proportion of about 2.7 per cent., which amounts to rather more than four ounces per gallon, or to a bushel in from 300 to 350 gallons.

The extraction of the chloride from sea water was formerly practised to some extent upon the southern coast of our own island: in Great Britain this mode of manufacture is now unimportant, though in the southern countries of Europe the preparation of bay-salt is still a branch of industry of some magnitude. In conducting this process the sea water is allowed to run into shallow pools, in which the water evaporates and the liquor becomes concentrated by the heat of the sun; crusts of the salt are formed, and are raked off from time to time: the rough crystals thus obtained furnish the *bay-salt* of commerce. The concentrated sea water, or *bittern*, is employed as a source of bromine.

Balard, who has devoted much attention to the study of these mother-liquors, has devised a method of extracting from them not only sodic sulphate, but also an important quantity of salts of potassium, in the form of a magnesio-potassic sulphate ( $\text{MgK}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ), as well as of a magnesio-potassic chloride ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). The process requires a careful attention to the temperature at which the crystallizations are effected. At temperatures below  $26^{\circ}.6$  ( $-3^{\circ}$  C.) the chloride of sodium still present in the brine decomposes the magnesic sulphate, magnesic chloride, and sodic sulphate being formed; whilst at tem-

peratures above  $100^{\circ}\cdot4$  ( $38^{\circ}\text{C.}$ ), a sparingly soluble sodio-magnesian sulphate ( $\text{Na}_2\text{Mg}_2\text{SO}_4\cdot6\text{H}_2\text{O}$ ) is formed. The following is the modification of Balard's plan, now adopted by M. Merle at Camargue (*Les Mondes*, January, 1866, p. 76): Sea water is concentrated in the salt-pans by spontaneous evaporation. Three different saline deposits are thus obtained; the first of these consists entirely of sodic chloride, and continues to be formed until the liquor acquires a density of  $1\cdot267$ . The second deposit, known as *mixed salt*, then makes its appearance, and continues to separate until the liquor attains a density of  $1\cdot3$ . It consists of common salt and magnesian sulphate in equal quantities. The third deposit, which is formed between the densities of  $1\cdot3$  and  $1\cdot32$ , is the *summer salt*. It contains the whole of the potash, partly in the form of magnesio-potassic sulphate, partly as magnesio-potassic chloride, mixed with sodic chloride and magnesian sulphate. The mixed salt is redissolved, and the concentrated solution cooled down artificially by the use of Carré's refrigerator (*note*, Part I. p. 339) till the temperature falls to  $0^{\circ}$  ( $-18^{\circ}\text{C.}$ ). As the liquor passes through the refrigerator, crystallized sodic sulphate is deposited in nearly a pure state, and is dried in a centrifugal hydro-extractor. The mother-liquor retains magnesian chloride, and is preserved. The crude *summer salt* is redissolved in a small quantity of water heated to  $90^{\circ}$  or  $100^{\circ}\text{C.}$ ; and on cooling it deposits rather more than half the potash as potassio-magnesian sulphate ( $\text{K}_2\text{Mg}_2\text{SO}_4\cdot6\text{H}_2\text{O}$ ). The mother-liquor retaining chlorides of sodium and potassium with magnesian sulphate is cooled down to  $-15^{\circ}$  or  $-18^{\circ}\text{C.}$ , by which more sodic sulphate is separated. The saline liquor is finally boiled down to a sp. gr. of  $1\cdot331$ , and deposits nearly all the remaining sodic chloride. The hot liquor is run into shallow coolers, where it deposits the whole of the potash in the form of the magnesio-potassic chloride ( $\text{KCl}\cdot\text{MgCl}_2\cdot6\text{H}_2\text{O}$ ). On treating this with half its weight of water, the salt is decomposed, the deliquescent magnesian chloride is dissolved, together with one-fourth of the potassic chloride, and the solution is returned to be recrystallized with the fresh mother-liquor—while the undissolved potassic chloride is ready for sale after it has been dried.

Immense beds of common salt are met with in Cheshire, at Wielitzka in Poland, and at Cardona in Spain. It has also recently been found in abundance in the north of Ireland, near Belfast, and on the southern borders of the Durham coal-field. Near Northwich, the principal deposit of rock salt in England, the mineral occurs in two beds, situated one above another, separated by about 9 metres, or 30 feet, of clay and marl intersected with small veins of salt: the two beds together are not less than 18 metres or about 60 feet in thickness, 274 metres or 300 yards broad, and a mile and a half long. These beds occur in magnesian limestone. The celebrated and beautiful mine of Wielitzka contains sufficient salt to supply the entire world for ages. It is calculated that the mass of rock salt here is 500 miles in length, 20 miles broad, and not less than 1200 feet (366 metres) in thickness. This salt deposit occurs in the chalk formation.\* Sodic

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\* Some specimens of the salt from this mine decrepitate when thrown into water, owing to the escape of condensed gas ( $\text{CH}_4$ ; Rose), which is liberated during the solution of the crystals.



chloride is sometimes found crystallized, and is then termed *sal gem*, or *rock salt*. Where coal is cheap, the solubility of the chloride is frequently taken advantage of in diminishing the labour of raising the salt to the surface, water being let down into the bed of salt and allowed to remain till it has become saturated: it is then pumped out and the brine is boiled down and crystallized.

Some brine springs contain too small a proportion of salt to render it profitable to effect the evaporation by heat; the water in these cases is therefore concentrated by *graduation*, as at Salzburg: this process consists in exposing the brine, diffused over a large surface, to the air, by pumping it up to a height, and then allowing it to trickle slowly over large stacks of fagots, piled in suitable buildings screened from rain, but freely exposed to the prevailing wind: after this process has been repeated eight or ten times, the solution acquires a density of about 1.140, and is sufficiently concentrated to allow the evaporation to be finished as usual by the direct application of heat. In the first basin an insoluble precipitate, chiefly consisting of the sodio-calcic sulphate is deposited ( $\text{Na}_2\text{Ca}_2\text{SO}_4$ ), partly in the form of mud, or *schlot* as the Germans term it, partly in the form of a hard scale, which adheres to the bottom of the pan: when the liquor reaches a density of 1.236 it is decanted into another pan and evaporated; the crusts of salt are removed as they are formed.

The appearance of the salt varies according to the rate at which the evaporation is conducted; when the brine is boiled down rapidly, it furnishes the mealy, fine-grained salt used upon our tables; if evaporated more slowly, the hard, crystallized salt preferred for fishery purposes is obtained. The salt of commerce always contains a certain proportion of magnesian chloride, which gives it a slightly deliquescent character, and adds to the pungency of its flavour. It is stated, that when the proportion of magnesian chloride in the brine is considerable, the crystals of sodic chloride form a scum over the surface which much retards the evaporation. This inconvenience may be remedied by the addition of a quantity of sodic sulphate, which decomposes the magnesian chloride and converts it into sulphate.

*Properties.*—Sodic chloride has an agreeable saline taste. It crystallizes in colourless transparent cubes, which are anhydrous, soluble in about 3 parts of cold water, and scarcely more soluble at a temperature of  $212^\circ$  ( $100^\circ$  C.); the saturated solution has a sp. gr. of 1.205. Water at  $32^\circ$  ( $0^\circ$  C.) dissolves 35.5 per cent. of the salt, and 41.2 per cent. at  $229^\circ.5$  ( $109^\circ.5$  C.), the boiling point of the solution. When heated suddenly, the crystals decrepitate with violence; at a bright red heat they fuse, and by a stronger heat are converted into vapour. Sodic chloride is insoluble in pure alcohol, but is taken up in considerable quantity by dilute spirit. By exposing its aqueous solution to a tempera-

ture of about  $14^{\circ}$  ( $-10^{\circ}$  C.), it crystallizes in hexagonal tables, which contain  $2\text{H}_2\text{O}$ : as the temperature rises, the water is separated, the crystals fall to pieces, and become converted into a heap of minute cubes.

Sodic chloride is consumed in large quantities in the manufacture of the salts of sodium; it is extensively employed in glazing stoneware, and is an article of daily domestic use, being indeed an essential constituent of the food both of man and of animals, who languish if it be supplied in insufficient quantity. The process of salting meat is resorted to on account of the powerfully antiseptic qualities of sodic chloride. In this operation a large quantity of the nutritive juice of the meat is extracted, and this liquid when saturated with the salt forms the *brine*. Meat thus prepared is much less digestible and nutritious than fresh meat.

Sodic chloride, when fused with rather more than one-third of its weight of sodium in a current of dry hydrogen, furnishes a blue compound, supposed to be a subchloride,  $\text{Na}_2\text{Cl}$  (Bunsen).

(584) SODIC BROMIDE, or *Bromide of sodium* ( $\text{NaBr} = 103$ ; *Sp. Gr.* 2.34) is analogous to potassic bromide; it is soluble both in water and in alcohol, and crystallizes at temperatures above  $86^{\circ}$  ( $30^{\circ}$  C.) in anhydrous cubes. At lower temperatures it forms hexagonal tables with  $2\text{H}_2\text{O}$ .

(585) SODIC IODIDE, or *Iodide of sodium* ( $\text{NaI} = 150$ ; *Sp. Gr.* 3.45) crystallizes at temperatures above  $104^{\circ}$  ( $40^{\circ}$  C.) in cubes, which are anhydrous; but if crystallized at ordinary temperatures it yields large transparent, striated, oblique rhombic prisms, with  $2\text{H}_2\text{O}$ . Sodic iodide occurs native in sea-water in minute proportion, but small as this proportion is, it furnishes the commercial supply of iodine: many marine plants appropriate it to their nutrition, and when these plants are burned, the iodide remains in the residue: the ash thus obtained goes by the name of *kelp*. A ton of good Irish kelp from drift-weed furnishes about 8 lb. of iodine.

(586) SODIC SULPHATE, or *Sulphate of sodium* ( $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O} = 142 + 180$ ); *Sp. Gr. anhydrous*, 2.597; *cryst.* 1.469; *Comp. in 100 parts* of dry salt,  $\text{Na}_2\text{O}$ , 43.67;  $\text{SO}_3$ , 56.33; of crystallized salt,  $\text{Na}_2\text{O}$ , 19.25;  $\text{SO}_3$ , 24.84;  $\text{H}_2\text{O}$ , 55.91.—This salt has long been known under the name of *Glauber's salt*. It crystallizes usually in long four-sided prisms, terminated by dihedral summits. It is remarkably efflorescent, and loses the whole of its 10 atoms of water by mere exposure, at common temperatures, to the atmosphere. It has a saline, bitter taste, and is occasionally used medicinally as a purgative.

The solubility of sodic sulphate in water offers some remarkable anomalies (55), which have been the subject of many inquiries, the most complete of which are those of Löwel.\* It has

\* Three forms of sodic sulphate may be obtained in crystals—viz. 1. the anhydrous sulphate; 2. the ordinary crystallized sulphate with  $10\text{H}_2\text{O}$ ; and 3.

already been mentioned (74) that a boiling saturated solution of this salt, if closed hermetically, may be kept for months without crystallizing, but the moment that air is admitted, the whole becomes semi-solid, from the sudden formation of crystals through the mass. It is most probable that the salt exists in the super-saturated solution in the form of the anhydrous salt, and that crystallization occurs when any circumstance occasions the formation of the less soluble 10-atom hydrate. The crystallization of such a solution may, for example, be instantly determined by dropping in a fragment of the sulphate, or by contact with a rod of glass or of metal. If, however, the glass rod or the metallic wire be boiled with water, and allowed to cool under water or in a closed vessel, kept chemically clean in short (Tomlinson), it

the hydrate with  $7\text{H}_2\text{O}$ , which crystallizes in rhombic prisms. Each of these varieties has a specific solubility. A 10-atom hydrate is the least soluble, and the 7-atom hydrate the most so of the three forms. The following table (Löwel, *Ann. de Chimie*, III. xlix. 50) exhibits the varying solubility of each form of sodic sulphate, as the temperature rises :—

100 Parts of Water when saturated contain, of

Temperature.		Anhydrous salt.		Salt with $10\text{H}_2\text{O}$ .		Salt with $7\text{H}_2\text{O}$ .		
° C.	° F.	with Anhydr. = $10\text{H}_2\text{O}$ .		with Anhydr. = $10\text{H}_2\text{O}$ .		with Anhydr. = $7\text{H}_2\text{O}$ = $10\text{H}_2\text{O}$ .		
0°	32			5'02	12'16	19'62	44'84	59'23
11'67	53'0			9'00	23'04	30'49	78'90	112'73
13'30	55'9			13'20	35'96	37'43	105'79	161'57
17'91	64'4	53'25	371'97	16'80	48'41	41'63	124'59	200'00
25'05	77'1	52'76	361'51	19'40	58'35	44'73	140'01	234'40
28'76	83'8	51'53	337'16	28'00	98'48	52'94	188'46	305'28
30'75	87'3	51'31	333'06	30'00	109'81	54'97	202'61	411'45
31'84	89'3	50'37	316'19	40'00	184'09			
32'73	90'9	49'71	305'06	50'76	323'13			
33'88	93'0	49'53	302'07	55'00	412'22			
40'15	104'3	48'78	290'00					
45'04	113'1	47'81	275'34					
50'40	122'7	46'82	261'36					
59'79	139'6	45'42	242'89					
70'61	159'3	44'35	229'87					
84'42	184'0	42'96	213'98					
103'17	217'7	42'65	210'67					

From this table it appears that the solubility of the anhydrous salt decreases from  $17^{\circ}91$  C. to the boiling-point ( $103^{\circ}17$  C.) of the solution. Below  $17^{\circ}91$  C. the molecular constitution of the salt is changed, a saturated solution depositing in vessels from which air is excluded, crystals of the 7-atom hydrate, 100 parts of water at  $17^{\circ}91$  C. retain as much as 53'25 of the anhydrous salt, whilst at the boiling-point only 42'65 parts are held in solution. Hence if a solution saturated at  $17^{\circ}9$  C. be simply heated to boiling, without allowing any loss of

may be introduced into the supersaturated solution without causing the crystallization of the salt.

Crystallized sodic sulphate is soluble in hydrochloric acid, with great depression of temperature. A convenient freezing mixture is obtained by pouring 5 parts of the commercial acid upon 8 of the crystallized sulphate.

Native sodic sulphate, to which the name of *Thénardite* has been given, has been met with nearly pure not far from Madrid, deposited at the bottom of some saline lakes, in anhydrous octohedra. It has likewise been found, not far from the same place, combined with calcic sulphate, as *Glauberite*, in anhydrous oblique prisms ( $\text{Na}_2\text{Ca}_2\text{SO}_4$ ).

Crystallized sodic sulphate also frequently occurs in needles as an efflorescence upon plaster, and upon brickwork in damp situations.

*Preparation.*—Sodic sulphate is made from oil of vitriol and

liquid by evaporation, it will deposit in hard, gritty, anhydrous crystals more than one-fifth of the salt which it previously held in solution.

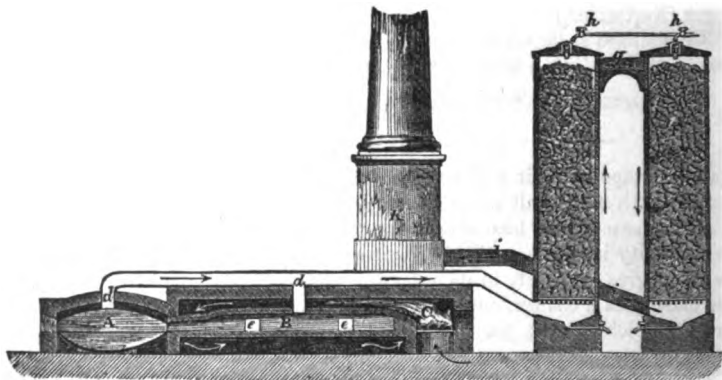
In the case of the least soluble form of the sulphate, the 10-atom hydrate, the solubility increases until the temperature reaches  $33^{\circ}\text{C}$ ., at which point the salt begins to liquefy in its water of crystallization: its molecular constitution then undergoes a change, and it becomes gradually converted into the anhydrous variety, which at that particular temperature has a lower solubility than the hydrated salt, and consequently is partially separated in crystalline grains.

The hydrate with  $7\text{H}_2\text{O}$  is more soluble than either of the foregoing forms; but under ordinary circumstances it cannot exist in contact with the atmosphere, and is only deposited from supersaturated solutions in closed vessels, or in flasks which have been allowed to cool covered with small capsules, so as to prevent the entrance of particles of dust or of foreign matter. Crystals of the 7-atom hydrate may also be obtained by pouring a boiling solution of the sulphate into a capsule and allowing it to cool under a bell-glass, over a vessel of calcic chloride. In whatever mode the crystals of the 7-atom hydrate have been produced, they undergo change from very slight causes, and become white and opaque with evolution of heat, either when exposed to the air, or when the solution is allowed to crystallize around them, or when touched with a glass rod. The solubility of the 7-atom hydrate rises with the temperature, as is shown in the table; but this form of the salt cannot exist at temperatures above  $29^{\circ}\text{C}$ .; for when heated to this point its crystals begin to liquefy in their water of crystallization; and, in consequence of a molecular change, crystals of the anhydrous variety are deposited.

From the foregoing details it will be easy to perceive why it is that a hot solution of the sulphate deposits crystals so slowly:—When a solution of sodic sulphate, saturated at its boiling-point, is poured into an open capsule, a film of crystals of the anhydrous sulphate is formed at first upon its surface, owing to the rapid evaporation of a portion of the solvent. No crystals, however, are deposited in the body of the liquid until the temperature has fallen to about  $33^{\circ}\text{C}$ . The film of crystals first formed is gradually redissolved, and crystals of the 10-atom hydrate are formed as the temperature continues to fall. If the solution be evaporated at temperatures above  $34^{\circ}\text{C}$ ., acute rhombic octohedra of the anhydrous salt are produced: but if a boiling saturated solution be allowed to cool in closed vessels, no crystals are deposited until the temperature falls to  $17^{\circ}\text{C}$ ., when oblique rhombic prisms of the 7-atom hydrate are formed.

common salt in enormous quantities, under the name of *salt-cake*, as a preliminary step in the manufacture of soda ash. The operation is carried on in a reverberatory furnace, connected with an apparatus for condensing the hydrochloric acid, which, till within the last few years, was allowed to escape into the atmosphere, to the serious injury of vegetation in the surrounding district. One of the best forms of furnace is shown in section in fig. 344: the course of the flues, however, is not exactly such as

FIG. 344.



is there represented: A, the smaller of the two compartments which compose the furnace, is of cast iron; into this (the *decomposer*) from 5 to 6 cwt. (about 250 or 300 kilos.) of common salt are introduced, and rather less than an equal weight of *brown* sulphuric acid, of specific gravity 1.78, is gradually mixed with it, a gentle heat being applied to the outside; enormous volumes of hydrochloric acid gas are disengaged, and pass off by the flue, d, to the condensing towers, E and F; these towers are filled with fragments of broken coke or stone, over which a continuous stream of water is caused to trickle slowly from h, h. A steady current of air is drawn through the furnace and condensing towers, by connecting the first tower with the second, as represented at g, and the second tower with the main chimney, k, of the works. In the first bed of the furnace, about half the hydrochloric acid is expelled from the salt: the pasty mass thus produced is then pushed through a door for the purpose into the *roaster*, or second division, B, of the furnace. In this state it consists of a mixture of acid sulphate of sodium and undecomposed salt. The reaction in the first bed of the furnace may be represented as follows;  $2\text{NaCl} + \text{H}_2\text{SO}_4 = \text{NaCl} + \text{NaHSO}_4 + \text{HCl}$ .

In the second stage of the operation a higher temperature is

required; the acid sulphate of sodium then reacts upon the unchanged chloride, and the conversion into normal sodic sulphate is complete; thus  $\text{NaCl} + \text{NaHSO}_4 = \text{HCl} + \text{Na}_2\text{SO}_4$ . The hydrochloric acid gas, as it is liberated from B, passes off through the flue, d, and is carried on to the condensing towers. Heat is applied to the outside of the roaster, B; the smoke and products of combustion circulate in separate flues around the chamber, in the direction indicated by the arrows, but never come into contact with the salt-cake in B.

*Sodic tripotassic disulphate* ( $\text{NaK}_2\text{S}_2\text{O}_6$ , Penny; *Sp. Gr.* 2.668).—This double salt is anhydrous; it may be formed by dissolving the two salts in water and evaporating. Gladstone has shown that the employment of a large excess of sodic sulphate does not alter the composition of the salt, the excess of sodic sulphate crystallizing in its usual form.

It is obtained upon a large scale from kelp liquors during the manufacture of iodine, and is known under the name of *plate sulphate*, from the manner in which it is deposited in hard crystalline layers or plates, upon the sides of the crystallizing vats. During the act of crystallizing it emits vivid scintillations of phosphorescent light: this phosphorescence is most striking when the temperature is near  $104^\circ$  ( $40^\circ \text{C.}$ ). A very brilliant effect is produced by dashing a pailful of the warm mother-liquor upon a crop of crystals in a vat from which the mother-liquor has been drained off a few hours previously.

*Hydrosodic sulphate*, *Acid sulphate of sodium*, or *Bisulphate of soda* ( $\text{NaHSO}_4 = 126$ ; *Sp. Gr.* 2.742) corresponding to the hydrotassic sulphate, may be formed. It is more easily deprived of basic hydrogen by heat than the acid sulphate of potassium;  $2\text{NaHSO}_4$  yielding  $\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ . The anhydro-salt, by a stronger heat loses its sulphuric anhydride, and may hence be employed as a convenient source of this anhydride (416).

(587) *SODIC SULPHITE*, or *Sulphite of sodium* ( $\text{Na}_2\text{SO}_3$ ,  $10\text{H}_2\text{O} = 126 + 180$ ; *Sp. Gr.* 1.736), is now prepared largely under the name of *antichlore*, for the purpose of removing the last traces of chlorine from the bleached pulp obtained from rags in the manufacture of paper. It is procured by passing sulphurous anhydride, obtained by the combustion of sulphur in air, over moistened crystals of sodic carbonate, so long as the acid gas is absorbed; the mass is dissolved in water and crystallized. Sodic sulphite forms efflorescent, oblique prisms, which fuse at  $113^\circ$  ( $45^\circ \text{C.}$ ); they are soluble in about 4 parts of cold water: the solution has a slightly alkaline reaction and a sulphurous taste.

A *Hydrosodic sulphite*, or *Acid sulphite of sodium*, may be obtained in crystals, either as ( $\text{NaHSO}_3$ ) or with  $4\text{H}_2\text{O}$ .

(588) *SODIC NITRATE*, *Nitrate of sodium*, or *Cubic nitre* ( $\text{NaNO}_3 = 85$ ; *Sp. Gr.* 2.26), occurs abundantly from 0.6 to 1.0 metre below the surface of the soil near Iquique, in the district of Atacama, in Peru. It is a somewhat deliquescent salt, and is soluble in about twice its weight of cold water: it crystallizes in

obtuse rhombohedra, and has a cooling, saline taste. When heated, it fuses at  $591^{\circ}$  ( $310^{\circ}5$  C.), and at a higher temperature it undergoes decomposition. It is employed in the manufacture of nitric and sulphuric acids, but from its deliquescence cannot be substituted for potassic nitrate in gunpowder. It is frequently used as a manure, as in top-dressing barley. Large quantities of sodic nitrate are converted into saltpetre by treating the sodic nitrate with potassic chloride in equivalent quantity. The sodic chloride crystallizes out of the concentrated boiling solution, and the nitre is deposited on cooling.

(589) SODIC CARBONATE, or *Carbonate of sodium* ( $\text{Na}_2\text{CO}_3$ ,  $10\text{H}_2\text{O} = 106 + 180$ ); *Sp. Gr., anhydrous, 2.509, cryst. 1.454*; *Comp. in 100 parts of dry salt,  $\text{Na}_2\text{O}$ , 58.49;  $\text{CO}_2$ , 41.51; cryst.  $\text{H}_2\text{O}$ , 62.93;  $\text{Na}_2\text{O}$ , 21.68;  $\text{CO}_2$ , 15.39.*—The preparation of this salt constitutes one of the most important branches of chemical manufacture in this country, immense quantities of it being consumed in the production of glass, in the fabrication of soap, and in the preparation of the various compounds of sodium, besides a considerable consumption as a detergent by the calico-printer, as well as in the laundry for softening hard waters by precipitating the salts of calcium and magnesium. Compounds of sodium, from their lower price, are now substituted in a great number of cases in which those of potassium were formerly employed, but there are a few in which their substitution is not practicable: potassic nitrate is still required in the manufacture of gunpowder; in the finest varieties of glass, potash is used on account of the green tint occasioned by soda; and chlorate, the chromates, and tartrate of potassium, as well as the cyanogen compounds of potassium, still are preferred to the corresponding salts of sodium.

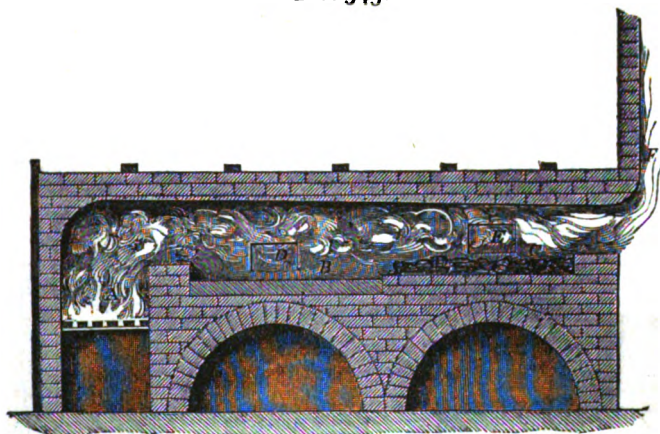
The greater portion of the sodic carbonate formerly employed was obtained from *barilla*, which is the ash furnished by burning marine plants. The *Salsola soda* was extensively cultivated for this purpose on the southern coast of Spain; and on being burnt, it yields a semi-vitrified mass, which contains from 25 to 30 per cent. of normal sodic carbonate. The *Salicornia* was cultivated for a similar purpose on the southern coast of France; but these sources of supply have almost entirely given way to a process by which the carbonate may be manufactured from sea-salt.

*Manufacture.*—In the process of manufacture a rough sodic sulphate is first formed, in the manner already described (586). This sulphate is then mingled with chalk and powdered coal in the proportion of about 3 parts of the sulphate, 3 of chalk, and  $1\frac{1}{2}$  or 2 of coal; this mixture is thrown, in quantities of about  $2\frac{1}{2}$

cwt., or 125 kilos., at a time, into a hot reverberatory furnace, and frequently stirred, until the mass is thoroughly melted.

The furnace, fig. 345, is constructed with two doors, D, E, and a double floor, B, C; one charge is introduced at the further door,

FIG. 345.



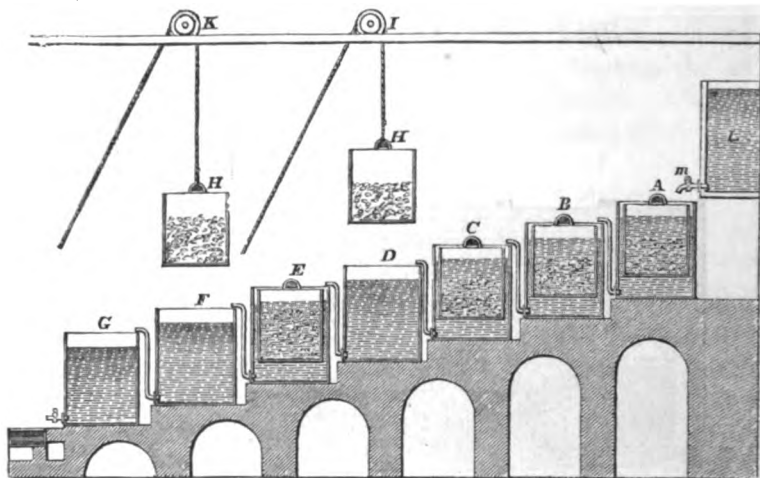
E, whilst another, nearer the fire, is fusing at B: towards the conclusion of the operation the mass melts, and effervesces violently from the escape of carbonic oxide gas, which burns with a greenish or yellow flame; the mass is stirred briskly for a few minutes, and when completely and tranquilly fused, is raked out into a square trough or mould; when cold, this loaf is turned out and forms *ball soda*, or *black-ash*, containing from 20 to 27 per cent. of pure soda, mixed with calcic sulphide, quicklime, and unburned coal. In order to extract the salts of sodium from it, the black ash is broken up into coarse fragments, and digested with warm water for six hours, in vats provided with false bottoms: this washing is systematically carried on till the soluble portions are extracted, the last washings being employed to act upon fresh portions of ball soda.

One of the forms of apparatus for the lixiviation of ball soda is shown in fig. 346. The principle on which it is constructed is simple, but it admits of extensive application; for in many cases much of the economy of a manufacturing process depends upon the systematic washing of the product in such a manner as to extract the largest amount of soluble matter by means of the smallest quantity of water, in order to reduce to a minimum the time and quantity of fuel required to effect the subsequent evaporations. In the case before us this is effected by placing the material for lixiviation—the black ash, in perforated sheet-iron vessels, H, H, which can be raised or lowered into outer lixiviating vessels, also made of iron, by means of the cords and pulleys I, K. When a charge is received from the furnace it is introduced into the lowest vessel, G, where it is submitted to the dissolving action of a liquid already highly charged



with alkali by digestion upon the black ash contained in the tanks above it : after a certain time this charge is raised by the rope from G into the tank F, where it is submitted to a weaker liquid, and so on, successively. The alkali at each stage

FIG. 346.



becomes more completely exhausted, and the residue is successively submitted to the action of weaker ley, till at length, in A, it is acted upon by water only, supplied from the cistern L. When fresh water is admitted from *m*, to the top of the vessel, A, as it is specifically lighter than the saline solution, it lies upon its surface, and gradually displaces the solution from A, through the bent tube, whilst the water takes its place; the liquid from A acts in a similar manner upon that contained in B; and this displacement proceeds simultaneously through each successive tier of the arrangement, until the concentrated ley flows off from C, and is transferred to the evaporating pans. A still more convenient arrangement, in which all the tanks are upon the same level, is now in common use in the alkali works of this country. The charge after it has once been introduced into the tank is not removed again until completely exhausted. By a suitable arrangement of pipes each tank can be made in succession the recipient of the fresh water, or of leys of gradually increasing strength derived from the neighbouring tanks; advantage being taken of the fact, that as the solution becomes more highly charged with the soluble material, the height of the column, or the water-level, in each successive vat stands progressively lower, until the liquid flows off saturated; and thus a continuous flow of liquid through the system is maintained. (*Chemical Technology, Richardson & Watts*, 2nd ed. vol. i. part iii. p. 267.)

Almost the whole of the sulphur originally present in the salt-cake is retained in the insoluble residue in the form of calcic sulphide, together with the excess of lime and coal employed. It accumulates at the soda works till it forms a mountain of *soda waste*, to the annoyance both of the neighbourhood and of the manufacturer.

The water for lixiviation must not be employed at a temperature exceeding  $111^{\circ}\cdot 2$  ( $44^{\circ}$  C.), otherwise the calcic sulphide is

decomposed into a mixture of sulph-hydrate, which is soluble, and hydrate of lime;  $2\text{CaS} + 2\text{H}_2\text{O}$  becoming  $\text{CaS}, \text{H}_2\text{S} + \text{CaO}, \text{H}_2\text{O}$ , and this sulph-hydrate immediately reacts upon the sodic carbonate, furnishing disodic sulphide and calcic carbonate, whilst the hydrosulphuric acid converts the caustic soda into disodic sulphide:  $\text{CaS}, \text{H}_2\text{S} + \text{Na}_2\text{CO}_3 + 2\text{NaHO} = 2\text{Na}_2\text{S} + \text{CaCO}_3 + 2\text{H}_2\text{O}$ . The black solution thus obtained is allowed to settle, and is then pumped up into large shallow iron pans, where it is evaporated by the waste heat from the black-ash furnaces. A large portion of the salt crystallizes during the ebullition, and is removed by means of perforated ladles. In order to convert the caustic soda which the solution contains into carbonate, it is evaporated to dryness, and after being mixed with about a seventh of its weight of sawdust, is roasted in a reverberatory furnace: most of the sulphur escapes during this operation in the form of sulphurous anhydride, the residue yields the *soda-ash*, or alkali of commerce, which contains about 56 per cent. of alkali,  $\text{Na}_2\text{O}$ , reckoned in the anhydrous state. If required in crystals, the crude carbonate thus obtained is redissolved, the liquid allowed to settle, and, while hot, is run into deep pans, capable of furnishing upwards of 100 kilos. or about a ton of crystallized carbonate. The liquid cools in the course of five or six days, and crystals of large size are formed; the mother-liquor, which is drained off by withdrawing a plug in the bottom, is then further evaporated down, and yields an ash of inferior quality.

The preparation of the commercial carbonate of soda, therefore, comprises three principal operations:—

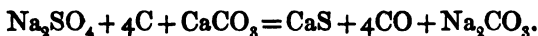
1st. The production of *salt-cake*, or crude sodic sulphate, from common salt, by the action of sulphuric acid.

2nd. The making of *black-ash*, or impure sodic carbonate, mixed with calcic sulphide, by deoxidation of the salt-cake after mixture with chalk, by means of carbon.

3rd. The preparation of *soda-ash*, or the separation of the sodic carbonate from the black-ash by lixiviating the latter in warm water and evaporating the solution to dryness.

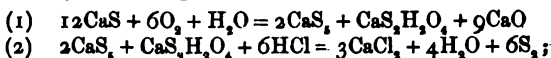
Of these operations the most remarkable is the preparation of the black-ash, by fusion of the sulphate with chalk and coal. The chemical changes which occur consist, first in the deoxidation of the salt-cake, and its conversion into disodic sulphide with evolution of carbonic oxide; and, secondly, in the formation of sodic carbonate and calcic sulphide by interchange of the constituents of the disodic sulphide and calcic car-

bonate.\* These reactions occur simultaneously, and may be represented in the following equation :—



An excess both of coal and of chalk is always employed in practice, as a good deal of coal burns off unavoidably, and an excess of chalk is needed to prevent the formation of a polysulphide of calcium. This chalk becomes quicklime in the furnace, and when the ball is lixiviated, the hydrate of lime at first produced is converted into carbonate, while caustic soda is formed in equivalent quantity (Gossage).

Many attempts have been made to recover the sulphur from the soda waste, the most successful of which consists in exposing the material in the tanks to oxidation by a current of air, the object being so to manage the operation that a mixture of soluble calcic persulphide and hyposulphite shall be formed, that on dissolving out from the sparingly soluble lime and its carbonate they may each deposit their sulphur on the addition of hydrochloric acid, according to reactions which may be thus represented :—



in practice the quantity of sulphur obtained is far less than the equations indicate, some sulphate and thionic compounds apparently being formed (803).

Various processes for obtaining sodic carbonate have, from time to time, been proposed, to supersede the one just described, which was invented by Leblanc; and some years ago works on a considerable scale were established, in which, upon a plan patented by Mr. Longmaid, by roasting iron or copper pyrites directly with sodic chloride, sodic sulphate was obtained without the preliminary manufacture of oil of vitriol, whilst chlorine is evolved. The reaction with iron pyrites may be thus represented:  $4\text{FeS}_2 + 16\text{NaCl} + 19\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{Na}_2\text{SO}_4 + 8\text{Cl}_2$ . A portion of the sulphur, however, always burns off in the form of sulphurous anhydride. By the employment of poor ores of copper and tin, it has been found possible to extract these metals with advantage from materials which would not otherwise have paid for working.

*Properties.*—Sodic carbonate has a nauseous alkaline taste; it is an efflorescent salt, usually crystallizing in large transparent rhomboidal prisms, which are soluble in any proportion in hot water, and even melt in their water of crystallization; they are also very soluble in cold water. The salt readily parts with its water, and melts at a red heat. If crystallized at a temperature of  $-4^\circ$  ( $-20^\circ \text{C.}$ ), an unstable hydrate with  $15\text{H}_2\text{O}$  may be obtained (Jacquelain). Mitscherlich has also obtained sodic carbonate crystallized with  $6\text{H}_2\text{O}$ . If crystallized above  $93^\circ.2$  ( $34^\circ \text{C.}$ ) the salt is deposited in forms derived from the square-based

\* Monosulphide of calcium is, as Mr. Gossage has pointed out, nearly insoluble in cold water. Oxysulphide of calcium, supposed by Dumas to be formed, and to furnish the condition required for rendering the sulphur insoluble, appears not to exist.

octohedron, which contain  $5\text{H}_2\text{O}$ ; whilst, if crystallized between  $158^\circ$  and  $176^\circ$  ( $70^\circ$  and  $80^\circ\text{C.}$ ), four-sided prisms are produced, which contain only  $\text{H}_2\text{O}$ . Solutions of the carbonate may, according to Löwel (*Ann. de Chimie*, III. xxxiii. 382), be obtained in the condition of supersaturation, by adopting precautions similar to those mentioned when speaking of the sulphate. The carbonate exhibits a maximum solubility at  $100^\circ\cdot4$  ( $38^\circ\text{C.}$ ); the decrease of solubility above this point arises from the formation of the monohydrate ( $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$ ), and this is deposited when a solution saturated at  $219^\circ\cdot2$  ( $104^\circ\text{C.}$ ) is concentrated by boiling.\*

(590) HYDROSODIC CARBONATE, *Acid carbonate of sodium*, or *Bicarbonate of soda* ( $\text{NaHCO}_3=84$ ; *Sp. Gr.* 2.192) is obtained by saturating a strong solution of the normal carbonate with carbonic acid; the solid crystallized carbonate also absorbs carbonic anhydride with considerable evolution of heat; and as the bicarbonate is less soluble than the carbonate, this process is employed for procuring pure carbonate from the commercial crystals; for on washing the powdered bicarbonate with cold water till the washings are free from sulphates and chlorides, a pure bicarbonate is obtained. This salt is also manufactured

\* This hydrate is more soluble in cold than in hot water, and becomes redissolved in the mother-liquor if allowed to cool. The supersaturated solution contains a hydrate with  $7\text{H}_2\text{O}$ . Löwel describes two modifications of this 7-atom hydrate, which differ in solubility and in crystalline form: one variety, *a*, is deposited in rhombohedral crystals, if a solution saturated at the boiling-point be corked whilst boiling, and allowed to cool down to between  $50^\circ$  and  $59^\circ$  ( $10^\circ$  and  $15^\circ\text{C.}$ ), but it is redissolved on raising the temperature to  $69^\circ\cdot8$  ( $21^\circ\text{C.}$ ); and on cooling down to between  $41^\circ$  and  $50^\circ$  ( $5^\circ$  and  $10^\circ\text{C.}$ ) the modification *b* is deposited in square tables. If cooled below  $4^\circ\text{C.}$  the solution gradually deposits the 10-atom hydrate, and the condition of supersaturation ceases. The following table gives a comparative view of the quantities of the 10-atom hydrate, and the two varieties of the 7-atom hydrate contained in 100 parts of the saturated solutions at different temperatures:—

100 parts of Water, when saturated, contain, of

Temperature.		$\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$ .		$\text{Na}_2\text{CO}_3\cdot 7\text{H}_2\text{O}(b)$ .			$\text{Na}_2\text{CO}_3\cdot 7\text{H}_2\text{O}(a)$ .		
$^\circ\text{C.}$	$^\circ\text{F.}$	Anhydr. salt.	Crystd. salt.	Anhydr. salt.	Crystd. with $7\text{H}_2\text{O } b$ .	Crystd. with $10\text{H}_2\text{O}$ .	Anhydr. salt.	Crystd. with $7\text{H}_2\text{O } a$ .	Crystd. with $10\text{H}_2\text{O}$ .
0	32	6.97	21.33	20.39	58.93	84.28	31.93	112.94	188.37
10	50	12.06	40.94	26.33	83.94	128.57	37.85	150.77	286.13
15	59	16.20	63.20	29.58	100.00	160.51	41.55	179.90	381.29
20	68	21.71	92.82	38.55	122.25	210.58	45.79	220.20	556.71
25	77	28.50	149.13	38.07	152.36	290.91			
30	86	37.24	273.64	43.45	196.93	447.93			
38	100.4	51.67	1142.17						
104	219.2	45.47	539.63						

upon a large scale by moistening the crushed crystals of sodic carbonate with water, and exposing them, upon cloths, to the depth of 2 or 3 inches (about 6 or 8 cm.), in stone or wooden boxes, to a current of gaseous carbonic anhydride: the water of crystallization is separated during the process, and the temperature rises considerably. The sesquicarbonate is first formed, and as the operation proceeds it is converted into the bicarbonate. The bicarbonate crystallizes in rectangular four-sided prisms, which require 10 parts of water for solution at ordinary temperatures. If its solution be heated, 4 atoms of the bicarbonate lose one of carbonic acid, and are converted into the sesquicarbonate,  $4\text{NaHCO}_3 = 2\text{Na}_2\text{CO}_3, \text{H}_2\text{CO}_3 + \text{H}_2\text{CO}_3$ ; and by continued boiling of the solution, and still more readily by heating the solid salt to redness, it is converted into the normal carbonate;  $2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$ .

A native *Sesquicarbonate of Sodium*\* ( $2\text{Na}_2\text{CO}_3, \text{H}_2\text{CO}_3 \cdot 2\text{H}_2\text{O} = 274 + 36$ ), which, however, always contains sulphate and chloride of sodium, has been long known in commerce as *trona* or *natron*; it is chiefly obtained as a saline efflorescence on the borders of some lakes, of which those of Egypt are the best known. Many other countries, however, such as those in the neighbourhood of the Black and the Caspian seas, as well as some parts of Thibet and of Siberia, also furnish this salt. It crystallizes in rhombic prisms, terminated by four-sided pyramids; it is less soluble than the normal carbonate, but more so than the bicarbonate, and has a feebly alkaline reaction.

The normal sodic and potassic carbonates, when melted together in the proportion of 1 atom of each ( $\text{K}_2\text{CO}_3 + \text{Na}_2\text{CO}_3$ ), readily combine and form a salt which fuses at a lower temperature than either of its components. On account of its ready fusibility, this mixture is preferred to either carbonate alone, as a means of decomposing siliceous minerals in analytical operations (576). If sodic carbonate be dissolved in a solution of potassic carbonate in excess, the solution, on evaporation, yields transparent crystals which, according to Marignac, consist of  $\text{NaKCO}_3, 6\text{H}_2\text{O}$ : this salt is decomposed if it be attempted to recrystallize its aqueous solution, normal sodic carbonate being deposited.

(591) PHOSPHATES OF SODIUM.—Phosphoric acid forms with sodium several crystallizable salts: some account has already been given of these compounds (448, 449, 450).

TRISODIC PHOSPHATE, or *Subphosphate of soda* ( $\text{Na}_3\text{PO}_4, 12\text{H}_2\text{O} = 164 + 216$ ); *Sp. Gr. cryst.* 1.622.—This salt is prepared from the rhombic phosphate by adding caustic soda to its solution till it feels soapy to the fingers. It crystallizes readily in small

\* The terms bicarbonate and sesquicarbonate are not strictly correct; but they are well understood, and convey with distinctness the ideas intended.

prisms, which effloresce in the air, and gradually absorb carbonic acid. A remarkable double salt of this phosphate with sodic fluoride ( $\text{NaF}, \text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ) was obtained by Briegleb, by fusing the rhombic or hydro-disodic phosphate with fluor-spar and sodic carbonate; and also by digesting powdered cryolite with a mixture of rhombic phosphate and caustic soda.

**HYDRO-DISODIC PHOSPHATE, or Rhombic phosphate of sodium** ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} = 142 + 216$ ); *Sp. Gr. cryst.* 1.586.—This salt is the one from which most of the phosphates are formed: it is the one which has been longest known, and is that commonly called 'phosphate of soda.' It is best procured by neutralizing with sodic carbonate the acid phosphate of calcium, prepared as directed for obtaining phosphorus (443): by this means calcic carbonate is precipitated, and allowed to subside; the clear liquid is then decanted from the precipitate, evaporated if necessary, and set aside to crystallize. Hydro-disodic phosphate forms large, transparent, efflorescent rhombic prisms: they have a cooling saline taste, and are soluble in 4 parts of cold water; at  $99^\circ$  ( $37^\circ.2$  C.) they fuse in their water of crystallization, and are therefore soluble in boiling water to an unlimited extent; the solution has a faintly alkaline reaction. It corrodes flint-glass bottles, and occasions the separation of white siliceous flakes from their surface. Clark found that when the solution of this salt is evaporated at temperatures above  $90^\circ$  ( $32^\circ.2$  C.), the salt crystallizes with 7 atoms of water, and is not efflorescent; in both forms it is isomorphous with the corresponding hydro-disodic arseniate. If heated to  $302^\circ$  ( $150^\circ$  C.), it loses all its water of crystallization; but if redissolved in water it may be obtained from its solution with all its characteristic properties. If a solution of this phosphate be mixed with free phosphoric acid, until it ceases to precipitate baric chloride, another phosphate is produced, *the sodio-dihydric phosphate*, formerly known as the *biphosphate of soda* ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O} = 120 + 18$ ); it crystallizes with difficulty in right rhombic prisms, and has a strongly acid reaction.

All these are tribasic phosphates; they precipitate argentic nitrate of a yellow colour.

**Tetrasodic phosphate, or Pyrophosphate of sodium** ( $\text{Na}_4\text{P}_2\text{O}_7, 10\text{H}_2\text{O} = 266 + 180$ ); *Sp. Gr. cryst.* 1.836.—If the rhombic phosphate be ignited it loses all its water, and on then treating it with water, a new tetrabasic salt is dissolved, which crystallizes in prisms. Its solution has an alkaline reaction, and yields a dense white precipitate with argentic nitrate, which is not changed by exposure to light.

SODIC METAPHOSPHATE, or *Metaphosphate of sodium* ( $\text{NaPO}_3 = 102$ ).—If microcosmic salt, or if the sodio-dihydric (acid tribasic) phosphate, or the dihydro-disodic phosphate (acid pyrophosphate), be heated to redness, all the volatile bases are expelled, the residue fuses to a clear glass, and on redissolving, sodic metaphosphate or monobasic phosphate of sodium is obtained. It forms a deliquescent and very soluble salt, which has a feebly acid reaction upon litmus. It cannot be obtained in crystals. The solution of this salt causes, with argentic nitrate, a white gelatinous precipitate, soluble in excess of the metaphosphate; with baric or calcic nitrate a similar gelatinous precipitate is formed. This salt is susceptible of various modifications by the application of different temperatures (450).

(592) BORAX, or *Acid borate of sodium*, ( $\text{Na}_2\text{O}_2\text{B}_2\text{O}_3, 10\text{H}_2\text{O} = 202 + 180$ ); *Sp. Gr. fused*, 2.367, *cryst.* 1.73; *Comp. in 100 parts, anhydr.*,  $\text{Na}_2\text{O}$ , 30.7;  $\text{B}_2\text{O}_3$ , 69.3; *cryst.*  $\text{Na}_2\text{O}$ , 16.23;  $\text{B}_2\text{O}_3$ , 36.65;  $\text{H}_2\text{O}$ , 47.12.—This well-known salt is produced in considerable quantities in various parts of the world, particularly in Thibet, whence for many years the principal part of the borax consumed was supplied. The crude borax, or *tincal*, is obtained by the spontaneous evaporation of the waters of the lakes whence it is derived, and occurs crystallized in flattened six-sided prisms, terminated by trihedral summits. These crystals are, however, very impure, being covered with a greasy coating, said to be derived from the skins in which they are imported. In order to remove this grease, the crystals are powdered, thrown upon a filter, and washed with a weak solution of caustic soda, which forms a soap with the grease, and dissolves it; the remaining salt is dissolved in water. Sodic carbonate equal to one-eighth of the weight of the borax is added to the solution; a copious precipitate of earthy impurities ensues, the liquid is cleared by filtration, and allowed to cool very slowly: the borax is deposited in rectangular or in six-sided prisms, containing  $10\text{H}_2\text{O}$ , one atom of which is probably basic.

A large quantity of borax is now manufactured from the boracic acid obtained from the lagoons of Tuscany, by saturating it with sodic carbonate, and allowing the salt to crystallize. In the course of this operation the crude boracic acid is mixed with about half its weight of soda-ash, and is thrown, in quantities of about 3 cwt. at a time, upon the floor of a reverberatory furnace; the mixture soon frits and effervesces, and must be well stirred during the process: a quantity of carbonic anhydride, of ammonia, and of organic matter which always accompanies the boracic

acid, is got rid of in this operation.\* The fritted mass is then lixiviated in deep iron boilers. Here the solution is allowed to remain at rest, in order to allow the impurities—which consist chiefly of alumina, calcic carbonate, and some silica—to subside: and the liquid, when brought to the sp. gr. 1.166, is drawn off into wooden tanks, lined with lead, where the solution cools very slowly. The large crystals in which borax is demanded for the market can be procured only by operating on very large masses of the salt, and allowing it to crystallize from a solution containing sodic carbonate in excess. Borax may also be obtained in octohedral crystals ( $\text{NaH}_2\text{BO}_3 \cdot 2\text{H}_2\text{O}$ ; sp. gr. 1.815), if the salt be allowed to crystallize at a temperature between  $176^\circ$  and  $131^\circ$  ( $80^\circ$  and  $55^\circ$  C.) from a solution of sp. gr. 1.256, to which about one-third more of sodic carbonate is added than is required to form the salt.

Borax has a feebly alkaline taste and reaction. The prismatic crystals are soluble in about half their weight of boiling water, and in 12 parts of cold water; they are slightly efflorescent. When heated, borax bubbles up, loses its water, and melts below redness into a transparent glass: this glass dissolves many metallic oxides, which often impart intense and characteristic colours to the bead. Borax is hence much used as a test before the blowpipe for recognizing the presence of certain metallic oxides. For this purpose a small crystal of borax is fused upon the end of a bent platinum wire, and a minute quantity of the substance to be tested is melted with the salt in the flame of the blowpipe: the colour of the glass varies according as the bead is heated in the oxidizing or in the reducing flame (494). The power which this salt possesses of dissolving the metallic oxides renders it advantageous, in the process of soldering oxidizable metals, to sprinkle the metallic surfaces with powdered borax; on the application of heat the borax melts as well as the solder, and the film of oxide which would otherwise prevent the adhesion is removed from the pieces of metal at the moment that the alloy is presented to unite them. Borax is used in the arts as a flux, and by the refiner in the melting of gold and silver. In making enamels, it is frequently added for the purpose of rendering the compound more fusible, and it is largely employed in fixing colours on porcelain.

Other borates of sodium may be formed, but ordinary borax

\* The ammonia which is lost by operating in this manner is in some works economized by dissolving sodic carbonate in water in tanks, adding the acid gradually, and conducting the vapours from the hot liquid into a reservoir containing sulphuric acid.



is the only salt of any practical importance; the tetraborate,  $2(\text{NaBO}_2, 3\text{HBO}_2), 7\text{H}_2\text{O}$ , crystallizes with great difficulty: a neutral borate may be obtained by fusing 1 atom of ordinary borax with 1 of sodic carbonate; it crystallizes in oblique, rhombic prisms ( $\text{NaBO}_2, 4\text{H}_2\text{O}$ ). They absorb carbonic acid from the air.

(593) SILICATES OF SODIUM.—When finely divided silica is gradually added to fused sodic carbonate, carbonic anhydride is evolved with effervescence, and a mixture of various silicates of sodium is formed. Fritsche obtained a silicate of the composition ( $\text{Na}_2\text{O}, \text{SiO}_2, 9\text{H}_2\text{O}$ ), by dissolving in a strong solution of caustic soda a quantity of silica equal in weight to the anhydrous soda present in the liquid: it crystallizes sometimes with 6, sometimes with 9, atoms of water. This silicate may also be obtained by fusing 2 parts of powdered flints with 3 of sodic carbonate. When a concentrated solution of sodic carbonate is boiled with finely divided silica, a large proportion of silica is dissolved: but the clear liquid, as it cools, deposits a gelatinous precipitate, consisting, according to Forchhammer, of  $\text{Na}_2\text{O}, 36\text{SiO}_2$ . Other silicates have been obtained, to which the proportions indicated by the formulæ ( $2\text{Na}_2\text{O}, 5\text{SiO}_2$ ) ( $\text{Na}_2\text{O}, 3\text{SiO}_2$ ) and ( $\text{Na}_2\text{O}, 4\text{SiO}_2$ ) have been assigned. It is difficult, however, to prove the existence of these compounds with the exception of the one last named. The silicate ( $\text{Na}_2\text{O}, \text{SiO}_2$ ) has the property of being dissolved by an excess of fused sodic carbonate, and the glass, which is clear and transparent while hot, becomes opaque on cooling; but the same silicate, if heated sufficiently with an excess of silica, melts and forms a homogeneous mixture, which yields a transparent glass on cooling, the fusibility decreasing as the proportion of silica increases, until, when the quantity of silica amounts to 9 atoms, the heat of a forge is required for its fusion. These silicates are all more or less soluble in boiling water.

A peculiar silicate, represented by the formula  $\text{Na}_2\text{O}, 4\text{SiO}_2$ , which has received the name of *soluble glass*, is prepared by melting together 8 parts of sodic carbonate (or 10 of potassic carbonate), with 15 of pure quartz sand and 1 part of charcoal (Fuchs): the charcoal by its tendency to form carbonic oxide, at the expense of the oxygen of the carbonate, facilitates the decomposition of this salt: a black glass is thus obtained, which is not soluble in cold water, but is almost completely dissolved by 5 or 6 times its weight of boiling water. Soluble glass is employed in fixing fresco colours, by the process known as *stereochromy*. The ground employed in this process for the reception of the colour consists of a mixture of lime and fine sand, cemented by a solu-

tion of soluble glass. The colours, ground up with water, are then applied, and a varnish of soluble glass is brushed over the whole. The material best adapted to this purpose consists of a mixture of this soluble glass solution with about one-fifth of its bulk of a solution of the monosilicate, both solutions being in a concentrated state (Fuchs).

Many metallic oxides—such as lime, magnesia, and zincic oxide, and their salts—are, as Kuhlmann has shown, acted upon by the solution of sodic silicate; calcic carbonate and other salts being converted by it into masses of great hardness and durability; double decomposition of the silicate and earthy salt occurring to a greater or less extent. By a further extension of this principle, Mr. Ransome has applied a solution of potassic or sodic silicate to the prevention of the decay of magnesian and other limestones which are exposed to the weather: a solution of the silicate is brushed over the surface of the stonework, and this is followed up by washing over the stone when dry with a solution of chloride of calcium, double decomposition occurs within the pores of the stone, the soluble chloride of sodium is formed, and may be removed by washing, whilst the surface becomes converted into the insoluble calcic silicate.

A very hard artificial sandstone is now also prepared by the same gentleman by mixing sand with a solution of calcic chloride, pressing it in a mould into the desired form, and then decomposing the calcic salt by silicate of soda, added in suitable proportions; the solution of silicate is forced into the mass by atmospheric pressure, and the sodic chloride is then washed out, water being also forced through the stone by atmospheric pressure.

A solution of sodic silicate as nearly neutral as possible is now very generally used as a substitute for cow-dung in preparing mordanted calico for dyeing. This constitutes one of the most important applications of the salt. This solution may be obtained of a sp. gr. of 1.53. It may be prepared either by fusing silica with sodic carbonate in the proper proportions, or by digesting calcined flints under pressure in a concentrated solution of caustic soda.

When heat is applied to the silicates of the alkalies, they do not at once become liquid, but pass through an intermediate viscous stage: they impart this viscosity, and the transparency which they preserve on cooling, to many other silicates if they are fused with them, and they destroy the tendency to crystallize on solidifying which the silicates of the earths and of the heavy metallic oxides possess. This property is of the highest importance to mankind, for upon it depend the most valuable properties of glass—ductility, which enables it to be moulded whilst in this intermediate state, and transparency, which renders it applicable to a

multitude of important uses. The silicates of the alkalis are unable alone to resist the action of water and other solvents sufficiently to fit them for many of the applications of glass; but when combined with silicates of the earths and certain metallic oxides, mixtures may be obtained after fusion which are no longer soluble in water or in acids.

### Glass.

(594) THE composition of glass differs considerably with the nature of the purposes to which it is destined, but it consists mainly of mixtures, in varying proportions, of silicates of potassium, sodium, calcium, barium, magnesium, aluminum, and lead, coloured by the addition of small quantities of different metallic oxides, particularly those of iron, manganese, cobalt, uranium, and gold.

The degree of fusibility of these different silicates varies considerably. The calcic and magnesian silicates fuse with great difficulty when heated *per se*: the most fusible compound contains 2 atoms of base to 3 of silica, the quantity of oxygen in the base, being to that in the silica as 1 is to 3. The ferrous sesquisilicate  $2\text{FeO}, 3\text{SiO}_2$ , and manganous sesquisilicate, are readily fused, and crystallize on cooling. Plumbic sesquisilicate  $2\text{PbO}, 3\text{SiO}_2$ , is still more fusible, and on cooling forms a yellow transparent glass. On the other hand, aluminic disilicate,  $\text{Al}_2\text{O}_3, 2\text{SiO}_2$ , is nearly infusible in the furnace. All these silicates, however, when mixed with each other, or with the silicates of the alkalis, melt at considerably lower temperatures, the fusing-point being generally much below that of the mean of the different silicates employed. The calcic and aluminic silicates are nearly infusible when separate, but they melt readily after they have been mixed together.

Many of the properties of glass are familiar to every one. It is a transparent brittle solid, more or less fusible, and just before fusion possessed of remarkable ductility, a property which enables the workman to fashion it into the numberless forms which luxury or convenience dictates. The different varieties of glass are not to be regarded as definite compounds, but as mixtures of various silicates in different proportions, with an excess of silica. It is generally found, however, in the best kinds of glass, that the mixtures are very nearly in such proportions that but little silica remains in the uncombined form. The proportion of silica to the bases is most conveniently expressed by ascertaining the proportion which the oxygen of the bases bears to that of the silica. The subjoined table gives the result of some analyses of the more important kinds of glass:—

*Composition of different Varieties of Glass in 100 parts.*

	Dumas.		Richardson.	Dumas.	Berthier.	Rowney.
	Bottle. French.	Window.		Plate.		Glass tube.
		French soft.	English.	French.	Venetian.	Bohemian.
Silica ...	53'55	69'65	66'37	73'85	68'6	73'13
Potash ...	5'48	...	...	5'50	6'9	11'49
Soda ...	...	15'22	14'23	12'05	8'1	3'07
Lime ...	29'22	13'31	11'86	5'60	11'0	10'43
Magnesia ...	...	...	...	...	2'1	0'26
Alumina ...	6'01	1'82	8'16	3'50	1'2	0'30
Oxide of iron ...	5'74	...	...	...	0'2	0'13
Oxide of man- ganese ... }	...	...	...	...	0'1	0'46
Ratio of the oxygen in the bases to that in the silica }	1 : 2	1 : 4	2 : 7	1 : 6	1 : 5	1 : 6

	Dumas.		Faraday.	Dumas.		
	Bohemian goblet.	German crown.	English flint.	Guinand's optical.	Strass.	Enamel.
Silica ...	69'4	62'8	51'93	42'5	38'1	31'6
Potash ...	11'8	22'1	13'77	11'7	7'9	8'3
Lime ...	9'2	12'5	...	0'5	...	...
Alumina ...	9'6	2'6	0'47	1'8	1'0	...
Oxide of lead ...	...	...	33'28	43'5	53'0	50'3
Oxide of tin ...	...	...	...	...	...	9'8
Oxides of iron and manga- nese ... }	...	...	0'27	...	As <sub>2</sub> O <sub>3</sub> B <sub>2</sub> O <sub>3</sub> } trace.	...
Ratio of the oxygen in the bases to that in the silica }	1 : 4	1 : 5	1 : 6	1 : 4	1 : 4	3 : 7

(595) *Glass in which Potassic and Calcic Silicates predominate.*—The potassic and calcic silicates are the principal components of the celebrated Bohemian glass, including the variety which is employed in the preparation of the hard glass of difficult fusibility, so much prized in the laboratory in the tubes used for the combustion of organic compounds: the composition of this glass may be represented approximatively by the formula  $(K_2O_3SiO_2 \cdot CaO_3SiO_2)$ , part of the potassium having its place supplied by sodium, and part of the calcium by magnesium, aluminum, and traces of iron and manganese. The more fusible glass which is employed in the manufacture of the beautiful

ornamental objects for which Bohemia has long been distinguished, contains aluminic silicate, with potassic and calcic silicates, in a proportion which approaches  $[3(\text{KCa})\text{O}, \text{Al}_2\text{O}_3, 12\text{SiO}_2]$ . The crown glass employed for optical purposes has nearly the formula  $\text{K}_2\text{O}, \text{CaO}, 4\text{SiO}_2$  (Dumas, *Ann. de Chimie*, II. xlv. 151). In the last two cases the proportion of oxygen in the bases to that in the silica is very nearly as 1 : 4.

In the finer kinds of glass, potash is always employed in preference to soda, because the glass made from soda, however carefully the materials are selected, has a bluish-green tinge, which is not observed when potash is used. The potash glass, however, is rather less brilliant than that which contains soda.

(596) *Glass consisting of Sodid and Calcic Silicates*.—French plate glass and ordinary window glass are the most important varieties of this description. Plate glass is very fusible, although the oxygen of the bases which it contains amounts only to about one-sixth of that of the silica. Soda produces a more liquid and fusible compound than potash. The addition of lime to glass diminishes its fusibility whilst it increases its lustre and hardness without affecting the colour. Care must be taken not to employ an excess of lime, for it is liable to render the glass milky-looking on cooling, although it may be perfectly transparent whilst hot.

Great care is required in the selection of the materials employed in the manufacture of the finer kinds of glass. The ingredients used in the plate glass of St. Gobain consist of 300 parts of white quartzose sand, 100 of dry sodic carbonate, 43 of lime, slaked by exposure to the air, and 300 of fragments of broken glass from previous meltings. The fuel employed in the furnace is wood.

These materials are intimately mixed, and then melted in a large, deep, conical crucible, in which, after they have been completely fused, they are allowed to stand at a high temperature for several hours, in order that the impurities may subside. Quantities of this mixture sufficient for casting a single sheet are then removed, by means of copper ladles, into a smaller square crucible, termed the *cuvette*.\* When the glass is thoroughly melted, the cuvette is removed from the furnace by a crane, and the glass is cast by pouring it upon a solid table of

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\* In the Thames Plate-glass Works, the glass is melted in the same pot as that from which it is poured in casting. The pots are cylindrical, and the fuel employed is coal.

cast-iron; along the edge of this table are ledges of metal, to regulate the thickness of the sheet of glass; the molten mass is immediately spread and formed into a plate by means of a heavy, hollow, metallic roller. These sheets are next annealed by being placed in a heated oven, and allowed to cool very slowly down to the temperature of the air—an operation which requires from a week to a fortnight for its completion. They are then levelled by cementing one plate with plaster of Paris upon a slab, and causing a second plate to move, by machinery, over the surface of the first, the grinding material being fine sand and water: a level surface having been thus obtained, it is smoothed by emery of gradually increasing fineness, and the final polish is given by friction with finely levigated colcothar or ferric oxide.

Window glass is made of a mixture of 100 parts of sand, with from 35 to 40 of chalk, 30 to 35 of soda ash, and from 50 to 150 of broken glass, or *cullet*. An equivalent amount of the cheaper sodic sulphate may be substituted in this mixture for the carbonate, for at a very elevated temperature the silica expels the elements of sulphuric anhydride; this decomposition may be facilitated by mixing the sulphate with about a tenth of its weight of charcoal; the sulphate is thus reduced to a lower state of oxidation, and the sulphur escapes in the form of sulphurous anhydride at a lower temperature than that required to expel the acid from the sulphate.

When sodic carbonate is used, the materials are first subjected to a heat insufficient completely to fuse the mass, and are *fritted* together, or heated until they agglomerate; moisture is thus completely expelled, and a part of the gaseous carbonic anhydride is got rid of; the frothing up of the mixture in the subsequent fusion, due to the expulsion of the gas, is also diminished, and the loss of alkali by volatilization is considerably lessened. The fritted mass is then transferred to other pots, and the temperature of the furnace is raised until complete fusion is effected. The mixture, after it has been thoroughly melted, is allowed to stand, in order that the bubbles of air may escape, and that the mass may become uniform in composition: the excess of sulphate or of chloride of sodium which may have escaped decomposition rises to the surface and is skimmed off, forming what the manufacturer terms *glass-gall* or *sandiver*. The glass is then allowed to cool until it assumes the pasty, tenacious condition required for the manipulations of the glass-blower.

(597) *Silicates of Aluminum, Calcium, Iron, Magnesium, and Sodium or Potassium*.—The inferior descriptions of glass which

are used for making wine-bottles, carboys, and other articles in which a dark colour is unimportant, consist of a mixture of these silicates. The materials employed are of a coarser kind than those used in the preceding varieties of glass. A ferruginous or ochry sand, mixed with soap-maker's waste, are common ingredients. Mr. Pellatt gives the following as a composition employed in making bottle glass:—Sand, 100 measures; soap-maker's waste, 80; gas-lime, 80; common clay, 5; and rock salt 3 measures. The ordinary English bottles are of an olive-green colour, produced by the presence of magnetic oxide of iron; while some of the German bottles are of a pale brown, resulting from a mixture of the oxides of iron and manganese. Sometimes baric sulphate is added with the view of rendering the glass more fusible. Bottle glass contains a smaller proportion of silica than any of the preceding varieties. One specimen analysed by Dumas, presented a composition which would be approximatively represented by the formula  $6[(CaK)O], (AlFe)_3O_3, 9SiO_2$ ; whilst in a second specimen the composition would be more nearly represented by  $6[(CaK)O] \cdot 2[(AlFe)_3O_3], 9SiO_2$ . The oxygen of the bases, in the first instance, is in the proportion to that of the silica as 1 to 2, and in the second case nearly as 2 to 3.

(598) *Devitrification: Réaumur's Porcelain.*—Bottle glass is particularly liable to become devitrified by slow cooling, and to be converted into what is termed *Réaumur's Porcelain*. In order to produce this effect, the glass may be imbedded in sand, or, still better, in a mixture of gypsum and sand, and heated up to a point sufficient to soften it, but just short of that required for its fusion. If it be now allowed to cool very slowly, it will be found to have entirely altered its aspect and properties; having become opaque and milk-white, and much resembling porcelain in appearance. It is now somewhat less fusible, and less liable to crack on the application of sudden changes of temperature, and is much harder than the glass from which it was procured. It is a bad conductor of heat, but conducts electricity to a considerable extent, being comparable in this respect to marble (Pelouze). This alteration appears to be due to the partial separation of certain silicates, particularly of the calcic and aluminic silicates, and their assumption of a more or less definite crystalline form. This crystallization is sometimes very beautifully and perfectly exhibited in the residues at the bottom of the glass-pots, which are allowed to cool down with great slowness and regularity. Nodules of opaque radiated crystals are there often found surrounded by a transparent glass. A mass of these opaque crystals, analysed by Dumas, presented a composition which corresponded with the formula,  $18[(CaNa)O], 2(Al_2O_3, 5SiO_2)$ ; whilst the transparent glass from which they had separated contained 3·5 per cent. less of silica, 1·4 less alumina, and a proportionately larger quantity of soda.

The devitrification of glass has been made the subject of experiment by Pelouze (*Chem. Gaz.*, Aug. 1855). He finds that the same sheet of glass may be devitrified, and again rendered transparent by fusion, many times in succession. Glass of any description may be devitrified, but the finer kinds of potash-glass exhibit this phenomenon with difficulty. The throwing in of a small quan-

tity of sand, or even of powdered glass, into a pot after it has cooled down to the viscid condition, greatly promotes the devitrification of the mass. The soluble soda-glass of Fuchs ( $\text{Na}_2\text{O}, 4\text{SiO}_2$ ) is especially liable to devitrification from crystallization.

(599) *Silicates of Potassium and Lead*.—The ordinary white glass in use in this country, commonly known as flint glass (the *crystal* of French writers), consists almost entirely of these silicates. Potash is used instead of soda in the preparation of flint glass, in order to avoid the bluish tint which is produced by soda in combination with oxide of lead. The oxide of lead imparts a greater degree of fusibility and density, as well as a high refractive and dispersive power; in consequence of which such glass, from its superior brilliancy, is better fitted for the manufacture of ornamental articles, and from its greater softness is more easily cut and polished. Lead glass has, however, the inconvenience of being readily scratched, and it is liable to tarnish and change colour, especially if the proportion of alkali be large. The alkalies corrode it slowly, and it becomes gradually blackened when left in contact with solutions of the sulphides. According to Faraday's experiments, English flint glass contains one-third or more of its weight of oxide of lead: it may be represented very nearly by the formula ( $\text{K}_2\text{O}, \text{PbO}, 6\text{SiO}_2$ ). But in a specimen from Newcastle, examined by Berthier, the proportion of silicate of lead was larger: this glass corresponded nearly to  $[2\text{K}_2\text{O}, 3\text{PbO}, 15\text{SiO}_2]$ . The composition of flint glass, however, is liable to considerable variation, even in different parts of the same pot, the lower portions having generally a greater density than those in the upper part of the pot. This arises from the density of the oxide of lead being much greater than that of the other materials, so that it is extremely difficult to preserve a uniform mixture. Faraday found, for example, that glass taken from the top of pots not more than 15 cm., or six inches deep, might have a density of 3·28, while that from the bottom might have a density of 3·85: in one instance the glass at the top had a density of 3·81, that at the bottom of 4·75; and though these are extreme differences, there is no doubt that considerable variations occur in every pot of glass made in the usual way. This variation in the density of the glass occasions great inconvenience in its application to the construction of optical instruments, owing to the difference of its refracting power in different portions of the same mass; and many endeavours have been made to overcome these defects. A lead glass of still higher refracting power was made by Guinand, in which the proportion of lead was very large, the formula being very



nearly  $[2K_2O, 3PbO, 10SiO_2]$ , the proportion of oxygen in the bases being to that in the silica as 1 to 4: its specific gravity was 3.61. Faraday (*Phil. Trans.*, 1830, p. 42) proposed, for a similar purpose, a compound of plumbic silicate and borate, the density of which is 5.44: this glass has a pale lemon-yellow tint, and consists of  $[3(PbO, SiO_2), 3PbO, 2B_2O_3]$ . Of late years a zincic borosilicate has been introduced by Maez and Clemandot into the glass used for optical purposes, with considerable success.

Much of the success in the preparation of glass for optical purposes depends upon the selection of pure materials, and also on their complete incorporation. The plan which succeeds best in attaining the latter object was introduced by Guinand. After the fusion is complete, the melted glass is thoroughly stirred with a paddle of crucible clay; the crucible and its contents are then allowed to cool down slowly in the furnace; when cold, the pot is broken, and by means of a wire and sand, kept wet, the mass of glass is cut *horizontally* into slices; in this way pieces of uniform density may generally be obtained. A good optical glass may be made from a mixture of 100 parts of pure sand, 100 of minium, and 30 of refined pearlash.

The oxide of lead which is employed in the manufacture of flint glass is not ordinary litharge (897), but minium, or red lead (898), which is a higher oxide of lead, and is prepared with care from pure lead. The proportions of the materials usually employed in the manufacture of flint glass are, 300 of fine white sand, such as that from Lynn on the coast of Norfolk, or from Fontainebleau, 200 of minium, and 100 of refined pearlash, with about 30 parts of nitre. In all cases the selection of materials for the melting-pot is of high importance. These pots are best made of an infusible clay, such as that from Stourbridge, which contains but little lime and iron: 5 parts of clay and 1 part of ground burnt pots are trodden into a mass by the workman, and allowed to stand for three or four months: the mixture is then carefully wrought into pots about four inches (10 cm.) thick, great care being taken to exclude air-bubbles. The pots are allowed to dry for several months in a warm room, after which they are removed to an annealing oven, where they are raised very gradually to the temperature of the furnace. Flint glass is always made in pots which are arched over at top, and have an opening at the upper part of one side for the introduction of the charge and the withdrawal of the glass: they are set in the furnace in such a manner as to prevent the access of smoke and combustible gases to the interior, which would endanger the reduction of the oxide of lead to the

metallic state. Plate glass, crown glass, and the other varieties of glass, are made in open crucibles. The alumina, which is contained even in the finest glass, is chiefly derived from the action of the vitrified materials upon the clay of the pots.

(600) *Coloured Glasses*.—For the purpose of producing imitations of precious gems, a lead glass of still higher refracting power, termed *paste*, or *strass*, is employed, the proportion of oxide of lead exceeding 53 per cent.; the composition of this substance is very nearly represented by the formula  $[K_2O, 3PbO, 8SiO_2]$ , the proportion of oxygen in the bases being one-fourth of that present in the silica. A little borax is often added to this glass to increase its fusibility. Glass of this description, when properly cut, is employed to imitate the diamond. The yellow colour of topaz is given to the strass by the addition of about 1 per cent. of ferric oxide, or by a mixture of 4 per cent. of antimonious oxide with a minute proportion (0.1 per cent.) of purple of Cassius. The brilliant blue of sapphire is imitated by adding a small quantity of cobalt oxide.

It is, indeed, a property of glass to dissolve small quantities of many of the metallic oxides without losing its transparency; but the glass becomes coloured with more or less intensity, and with different hues, according to the nature of the metallic oxide employed. Ferrous oxide appears to pass into the condition of magnetic oxide, which even in small quantities, communicates colours which vary from a pale green to a deep bottle-green, according to the proportion in which it is present: ferric oxide, on the contrary, has but feeble colouring power, unless present in considerable quantity, when it produces a yellow colour; manganoous oxide is nearly colourless, but the sesquioxide communicates a violet tint to the glass. Advantage is taken of the knowledge of these facts in preparing colourless glass: ferrous oxide, in minute quantity, is a frequent impurity in the materials used, and it produces the green tinge often observed in ordinary glass: a minute quantity of black oxide of manganese corrects this; it imparts oxygen to the magnetic oxide of iron, which thus becomes converted into the colourless sesquioxide, whilst the manganese itself being reduced to the state of protoxide exerts no injurious colouring effect. A little nitre or arsenious anhydride is sometimes added to glass instead of oxide of manganese, with a similar effect in converting the iron into sesquioxide. The manganese is, however, the more effectual agent; this may arise, as Liebig suggests, from the circumstance that the colours produced by the iron and manganese are each complementary to the other.

Chromic oxide imparts an emerald-green tinge to glass; cobalt oxide a deep blue. A mixture of the oxides of cobalt and manganese gives a black glass; cupric oxide ( $\text{CuO}$ ) produces a green; cupreous oxide ( $\text{Cu}_2\text{O}$ ) an intense ruby red; whilst the sparkling appearance of aventurine is due to the dissemination of tetrahedral crystals of reduced metallic copper through the mass. Uranic oxide communicates to the glass a peculiar opalescent yellow; different shades of yellow are also produced by oxides of silver and antimony, and by finely divided charcoal; and a compound of gold with oxide of tin (purple of Cassius) gives a magnificent ruby glass.

Sometimes glass is *flushed*, or superficially coated with the coloured portion. A mass of colourless glass is in this case taken by the workman upon the end of his blowing tube, and then dipped into a pot of the coloured glass—ruby, blue, or opal, as the case may be; on blowing out the lump of glass, a vessel is obtained the exterior layer of which is coloured, whilst the inner layer consists of colourless glass.

Painting on glass is effected by means of a very fusible glass, which when melted gives the required tint; this glass is reduced to a very fine powder, and worked up with turpentine into a pigment: it is then applied with a pencil to the surface of a sheet of ordinary glass. The painted glass is afterwards subjected to a heat which is sufficient to melt the coloured glass, but is not intense enough to soften the glass to which it is applied.

*Enamel* is the term given to an easily fusible glass, through which is disseminated an opaque white substance infusible at the temperature employed, such for example as the stannic oxide; a metallic ash is prepared by calcining at a low red heat a mixture of 1 part of tin with from 1 to 6 parts of lead, in a flat cast-iron vessel; the ash so obtained is mixed with sand and alkali, the proportions of which may vary considerably. In one recipe for the preparation of enamel given by Knapp, the ashes of 4 parts of tin and 10 of lead are directed to be ground up with 10 parts of powdered quartz and 2 of pure soda-ash. Other opaque bodies may be substituted for the stannic oxide in the preparation of enamel: in this manner bone-ash, antimonious oxide, and even arsenious anhydride, are sometimes employed to produce the opacity required. The enamel may be tinged of any desired colour by the suitable addition of metallic oxides. The enamel is applied with a brush to the surface to which it is to be attached, and is then fused by exposure to heat.

A modification of glass resembling enamel has been used to glaze cast-iron pots, as a substitute for tinning. It consists of powdered flints ground with calcined borax, fine clay, and a little felspar. This mixture is made into a paste with water, and brushed over the pots, after they have been scoured with diluted sulphuric acid and well rinsed in water; while they are still moist, they are dusted over with a glaze composed of felspar, soda-ash, borax, and a little stannic oxide. Having been thus prepared, the pots are next carefully dried, and finally the glaze is fused or *fired* under a muffle at a bright red heat. Plumbic oxide, though it

increases the fusibility of the glaze, should be carefully avoided, for it does not resist the action of acids in culinary operations.

(601) *Properties of Glass*.—Well-made glass is unacted upon by any acid or mixture of acids except the hydrofluoric, which destroys it by combining with its silica. But it is not absolutely insoluble, though it is generally considered to be capable of withstanding the action of water. If glass be powdered and moistened with water, the liquid will dissolve a small quantity of alkali, sufficient to turn turmeric-paper brown. Most varieties of powdered glass when exposed for some time to the air, were found by Pelouze to absorb carbonic acid in quantity sufficient to effervesce when treated with an acid, particularly if they had been kept moistened with water. If left long in water, or buried in moist earth, many kinds of glass become disintegrated slowly, and scale off in flakes which exhibit the brilliant colours of Newton's rings (116). This is particularly the case with the coarse glass used for wine bottles. Faraday found that some inferior kinds of bottle glass were destroyed rapidly by the action of diluted sulphuric acid.

At a high temperature water gradually decomposes glass; pieces of plate and window glass were suspended by Turner in the steam of a high-pressure boiler, and in the course of four months, specimens of plate glass one-fifth of an inch ( $5^{\text{mm}}$ ) thick were completely decomposed; and Faraday found that flint glass, under similar circumstances, was still more rapidly acted upon.

If glass be suddenly cooled after fusion, it becomes extremely brittle. When drops of melted glass are allowed to fall into water, they solidify in pear-shaped masses, which may be subjected without breaking to considerable pressure, if gradually applied; but if the tail of one of the drops, known as *Rupert's drops*, be suddenly nipped off, the glass flies to pieces with a kind of explosion, and is shattered to powder. This effect appears to be due to the unequal tension to which the particles composing the drop are subjected, owing to the sudden cooling of the outer surface of the glass, while the interior is still dilated: as the mass cools, the particles within, by adhesion to the external solid portion, are still kept in their dilated state; but a very slight disturbance of their relative position suffices to overcome their equilibrium, and when once the mass gives way at any one point, the cohesion of the whole is suddenly destroyed.

Similar changes occur if glass articles are allowed to cool rapidly by exposing them whilst red hot to the external air. Glass

objects of various descriptions, if their surface be but scratched, or if they be brought suddenly from a cold room into a warm one, will often crack and fall to pieces. In order to prevent this mishap, it is necessary to subject the different articles, after they have received their destined shape at the hands of the workman, to the operation of annealing, which is a very slow and gradual process of cooling, by which the parts are enabled to assume their natural position with regard to each other. Even then, since glass dilates considerably on the application of heat, and is likewise a bad conductor, a sudden and incautious elevation of temperature, such as that occasioned by pouring boiling water into a cold glass, often determines its fracture. Care is required during the process of annealing, especially with the coarser kinds of glass, not to raise the temperature too high; as otherwise devitrification to a greater or less extent would be liable to ensue.

(602) CHARACTERS OF THE SALTS OF SODIUM.—We have no good direct test for the salts of this metal, as it forms scarcely any insoluble compounds. Its most insoluble salt is what Fremy has termed sodic bimetantimoniate (853), which is deposited in transparent octohedra when a solution of freshly prepared *potassic bimetantimoniate* is added to a neutral solution containing sodium, provided that the liquid has been previously freed from all bases except the alkalies: 1 part of sodium in 10,000 of water will produce a precipitate with this test after twenty-four hours. In analysis, a salt of sodium is concluded to be present when the absence of every other metal has been proved, and yet a saline residue remains, which, with platinic chloride, gives yellow striated prismatic crystals ( $2\text{NaCl}, \text{PtCl}_4, 6\text{H}_2\text{O}$ ) by spontaneous evaporation. Andrews (*Chem. Gaz.* x. 378) has pointed out a property of this salt which admits of its identification in extremely minute quantities; a drop of the solution suspected to contain sodium is mixed with a minute quantity of a solution of platinic chloride, and allowed to evaporate in a warm place; if, before it is quite dry, it be placed in the field of the microscope, and examined by means of polarized light, minute crystals of the sodio-platinic chloride will be distinguished from the other salts with which they are accompanied, by their power of transmitting the polarized light, tinged with various colours, according to the thickness of the crystals. *Before the blowpipe* the salts of sodium are known by the intense yellow which they communicate to the outer flame, if a fragment be introduced at the point of the blue cone upon a loop of platinum wire; and this flame, if examined by the spectroscope, is seen to

consist of a pure yellow light exactly coincident in position with Fraunhofer's double line *D* in the solar spectrum, fig. 83, *Na*, Part I. p. 180.

The salts of sodium are in general more soluble than those of potassium; the sulphates of the two metals afford a striking instance of this difference: the sodium salts also often effloresce when exposed to the air, whilst those of potassium, on the other hand, frequently deliquesce, a fact well exemplified by the carbonates of the two metals.

§ III. LITHIUM: ( $L=7$ ); *Sp. Gr.* 0.5936; *Fusing-pt.* 356° (180° C.).

(603) LITHIUM, the metallic base of the third of the alkalis, is of comparatively recent discovery, and derives its name from *λίθος* (a stone), as it was at first found only in the mineral kingdom. It was supposed to be a very rare substance, but Bunsen and Kirchhoff have shown, by means of the method of spectrum analysis, that though sparingly it is widely distributed; they found it in many micas and felspars, in the ash of tobacco of many kinds, and in several mineral springs. The minerals of most frequent occurrence which contain lithium are the three which follow; they yield this alkali in proportion varying from 3 to 6 per cent. of their weight:—

Lepidolite, or lithia mica	...	...	[ $(LK)F$ ], $(Al_2O_3, 3SiO_2)$ ?
Triphane, or spodumene	...	...	$3(LNa)_2O, 4Al_2O_3, 15SiO_2$
Petalite ... ..	...	...	$3(LNa)_2O, 4Al_2O_3, 30SiO_2$

Metallic lithium is easily reduced from its fused chloride by means of an electric current obtained from four or six pairs of the nitric acid battery. The metal is of a white colour, and is fusible at 356° (180° C.). It is harder than potassium, but softer than lead, and admits of being welded by pressure at ordinary temperatures; it can be squeezed into wire, which, however, is inferior in tenacity to lead wire of the same dimensions. Lithium appears to be the lightest solid body known; it floats in naphtha, and has a density of only 0.5936. At high temperatures it is volatile, and may be distilled at a full red heat in a current of hydrogen. It cannot, however, be obtained by processes similar to those employed for potassium and sodium. A fragment of lithium burns upon a plate of mica with a very brilliant white light, emitting a heat sufficiently intense to melt a hole in the mica; when thrown upon water it swims and becomes oxidized, like sodium. If thrown into sulphuric or into nitric acid it usually takes fire.

(604) *Lithia* ( $L_2O=30$ ) was discovered by Arfwedson, in 1818. It may be extracted by carefully levigating the minerals that contain it, and igniting the fine powder with twice its weight of quicklime. The mass is treated with hydrochloric acid, then with sulphuric acid, and the lithic sulphate is dissolved out from the

calcic sulphate; the last traces of calcium are removed from the solution of lithic sulphate by ammonic oxalate. This solution may then be deprived of sulphuric acid, and converted into caustic lithia by the addition of baryta water; the solution on evaporation yields lithic hydrate (LHO).

Troost (*Ann. de Chimie*, III. li. 103) considers it to be more advantageous to melt 10 parts of powdered lepidolite with 10 of baric carbonate, 5 of baric sulphate, and 3 of potassic sulphate. The fused mass separates into two portions, a heavy transparent glass and a supernatant white slag; this white mass consists of a mixture of the sulphates of barium, potassium, and lithium, and contains nearly all the lithium. The sulphates of the alkali-metals are separated from that of barium by washing, and a portion of the potassic sulphate is removed by crystallization. The remaining potassic and lithic sulphates may be converted into chlorides by the addition of baric chloride, and the two chlorides separated by evaporating to dryness and digesting them in a mixture of equal parts of alcohol and ether, which dissolves the lithic chloride only.

*Lithic hydrate* (LHO) fuses easily below redness, and corrodes platinum vessels powerfully: silver capsules should therefore always be used in preparing it. This action upon platinum is one of the best indications of the presence of lithium. It appears to be due to the formation of an unstable *peroxide of lithium*, which imparts its oxygen rapidly to the platinum.

(605) *Lithic chloride*, or *Chloride of lithium* ( $\text{LiCl} \cdot 2\text{H}_2\text{O} = 42.5 + 36$ ), is fusible at a dull red heat: it crystallizes at temperatures above  $59^\circ$  ( $15^\circ \text{C.}$ ) in anhydrous octohedra; but below  $50^\circ$  ( $10^\circ \text{C.}$ ) in square prisms with  $2\text{H}_2\text{O}$ : it is one of the most deliquescent salts known. If its aqueous solution be evaporated at a high temperature, it loses a portion of its chlorine, whilst lithia is formed. Lithic chloride is very soluble in alcohol, and in a mixture of equal parts of alcohol and ether; as this mixture does not dissolve the chlorides of sodium and potassium, it may be used to separate chloride of lithium from these salts. I have found this chloride abundantly in a hot saline spring in Clifford United Mines, in Cornwall, where it occurs to the extent of 26 grains in the gallon, accompanied by a very large proportion of the chlorides of sodium and calcium, and a small amount of caësic chloride.

*Lithic sulphate*, or *Sulphate of lithium* ( $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} = 110 + 18$ ; *Sp. Gr.* 2.02), crystallizes in flat tables, which are very soluble in water. There appears to be no acid sulphate of lithium, though a potassio-lithic sulphate may be formed, consisting of  $\text{LKSO}_4$ .

*Tri-lithic phosphate*, or *Phosphate of lithium* ( $\text{Li}_3\text{PO}_4 = 116$ ), is one of the most characteristic salts of this alkali: it is insoluble in water containing phosphates of the alkalies, and in alkaline

solutions, but very soluble in acids even when very dilute. In order to prepare it, caustic soda is added to the solution of a pure salt of lithium till it has an alkaline reaction; hydro-disodic phosphate is added; the liquid is then boiled, and left for at least 12 hours. A heavy granular crystalline deposit of trilitic phosphate gradually occurs. This salt fuses with sodic carbonate to a glass which is transparent while hot, but becomes opaque on cooling; the transparency of the hot bead furnishes a distinction between trilitic phosphate and the phosphates of the earths, which furnish an opaque bead both when hot and when cold. The salt supposed by Berzelius to be a sodio-lithic phosphate, appears to have been a mixture, and not a definite compound.

*Lithic carbonate*, or *Carbonate of lithium* ( $\text{Li}_2\text{CO}_3=74$ ), is only sparingly soluble in water, but is rather more soluble in a solution of carbonic acid: it has an alkaline reaction upon turmeric. At a dull red heat it melts into a white enamel, and by prolonged ignition loses a large portion of its carbonic acid.

CHARACTERS OF THE SALTS OF LITHIUM.—Generally speaking the salts of lithium are remarkably fusible; many of them are very deliquescent. They have a burning saline taste, and are distinguished by yielding a white precipitate of lithic carbonate in cold concentrated solutions with *potassic carbonate*, but the precipitate disappears on adding water and applying heat; this reaction is less delicate when salts of ammonium are present. On the addition of *hydro-disodic phosphate* to solutions which are neutral or alkaline, trilitic phosphate is formed; it is soluble in the acids and in solutions of salts of ammonium. *Before the blowpipe* the salts of lithium communicate a purplish red colour to the flame, which is masked by the presence of salts of sodium in very small proportion. By means of the spectroscope the occurrence of very minute traces of lithium may be discovered by a brilliant crimson band, which has a refrangibility between that of the lines B and C of the solar spectrum. At very high temperatures a faint band in the orange may sometimes be seen. In these two lines the whole light of the lithium spectrum is contained when formed by the gas-flame of Bunsen's gas-burner, (fig. 83). When lithium salts are heated on platinum foil they corrode it rapidly.

§ IV. RUBIDIUM: ( $\text{Rb}=85.36$ .) *Sp. Gr.* 1.52; *Fusing-pt.*  $101^{\circ}3$  ( $38^{\circ}5$  C.).

(606) RUBIDIUM derives its name from *rubidus* (dark red), because the spectra of its salts, when volatilized in the colourless



flame of a Bunsen gas-burner, exhibit a remarkable pair of red lines, less refrangible than Fraunhofer's line  $\Lambda$  (Part I. fig. 83, *Rb*, p. 180). Rubidium was discovered in 1860 by Bunsen and Kirchhoff during their investigations on the spectra of artificial flames (Liebig's *Annal.* cxix. 107, and cxxii. 347). It is usually present in small quantity in lepidolite, and traces of it occur in many of the mineral springs of Germany. It has also been found by Grandeau (*Ann. de Chimie*, III. lxvii. 155) in minute quantity in beet-root, in tobacco, and in the ashes of a great variety of plants, being, though sparingly, yet very widely distributed. The separation of rubidium from other metals is founded upon the sparing solubility of the chloride of rubidium and platinum, by a method which will be described when speaking of the extraction of cæsium (608).

Metallic rubidium was extracted by Bunsen from the charred acid tartrate, 70 grammes of which when distilled furnished about 5 grammes of a brilliant silver-white metallic mass. It tarnishes rapidly on exposure to the air, becoming coated with a blue suboxide; in a few moments it takes fire spontaneously. At  $14^{\circ}$  ( $-10^{\circ}$  C.) it is soft, like wax; at  $101^{\circ}\cdot3$  ( $38^{\circ}\cdot5$  C.) it melts; and at a heat below redness it furnishes a blue vapour with a shade of green. Rubidium is decidedly more electropositive than potassium: when thrown upon water it takes fire and burns with a flame in appearance exactly resembling that of potassium.

(607) *Rubidia* ( $\text{Rb}_2\text{O} = 186\cdot7$ ) is a powerful alkaline base which may be obtained from the carbonate or sulphate in the form of hydrate ( $\text{RbHO} = 102\cdot3$ ) by processes resembling those adopted for potassic hydrate. It is very deliquescent, is soluble in alcohol, and absorbs carbonic acid with avidity.

*Rubidic chloride*, or *Chloride of rubidium* ( $\text{RbCl} = 120\cdot8$ ), crystallizes with difficulty in cubes; it is easily fusible, and is more soluble than potassic chloride, but is permanent in the air. With platinic chloride it forms a sparingly soluble double chloride ( $2\text{RbCl}, \text{PtCl}_4$ ) which requires 185 times its weight of boiling water for its solution. If fused rubidic chloride is submitted to electrolysis, the reduced metal is dissolved by the chloride and forms a smalt-blue subchloride.

*Rubidic sulphate* ( $\text{Rb}_2\text{SO}_4 = 266\cdot7$ ) crystallizes in hard, brilliant anhydrous prisms, isomorphous with those of potassic sulphate, but it is much more soluble than this salt. A true rubidium alum may be obtained in octohedral crystals by allowing a mixture of rubidic with aluminic sulphate to evaporate spontaneously. An acid sulphate of rubidium ( $\text{RbHSO}_4$ ) is also known.

*Rubidic nitrate* ( $\text{RbNO}_3 = 147\cdot3$ ) is a very soluble salt requiring 2·3 parts of water at  $50^{\circ}$  ( $10^{\circ}$  C.) for its solution. It crystallizes in dihexagonal prisms, terminated by dihexagonal pyramids.

*Rubidic carbonate* ( $\text{Rb}_2\text{CO}_3 = 230\cdot7$ ) is a deliquescent salt which may be obtained with difficulty in crystals with  $\text{H}_2\text{O}$ . It absorbs carbonic acid with avidity and furnishes a *hydro-rubidic carbonate*, or *bicarbonate* ( $\text{RbHCO}_3$ ) which crystallizes in brilliant

prisms that are permanent in the air and insoluble in alcohol. When heated they are converted into the normal carbonate, which by further elevation of temperature fuses easily.

CHARACTERS OF THE RUBIDIUM SALTS.—The salts of rubidium are distinguished from those of potassium with difficulty. The rubidio-platinic chloride is the most characteristic: by its sparing solubility in boiling water, it may be separated from the potassium salt, which is soluble in one-eighth of the quantity of water required for solution of an equal weight of the rubidium salt. The most certain test is the appearance of the flame in the spectroscope, which exhibits two characteristic lines in the red, less refrangible than that of potassium, and two lines in the blue, intermediate between those of cæsium and potassium.

#### § V. CÆSIUM: Cs=133.

(608) This metal derives its name from *cæsius*, sky-blue, in allusion to the two brilliant blue bands produced by it in the spectrum of a gas-flame in which its compounds are undergoing volatilization. It was discovered by Bunsen and Kirchhoff at the same time as rubidium (*Pogg. Annal.* cxiii. 337), which indeed it usually accompanies in very small quantity. Cæsium was originally discovered amongst the saline constituents of the Durkheim spring, the water of which contains about one five-millionth of its weight of a salt of cæsium, or about 1 grain in 140 gallons. Ordinary lepidolite contains only traces; but a variety of this mineral from Hebron, in the State of Maine, N.A., was found, by Johnson and Allen, to yield 0.24 per cent. of the metal. Still more recently, Pisani has found cæsium to the extent of 32 per cent. in a rare mineral named pollux, analogous to analcime, obtained from the island of Elba (*Comptes Rendus*, 18 April, 1864).

Böttger, in examining the salt obtained by evaporating down the mother-liquor of the Nauheim spring, discovered in it cæsium, rubidium, and thallium. He, indeed, recommends it as the cheapest source of the two new alkali-metals; they exist in the spring in the form of chlorides.

In order to obtain the compounds of cæsium, advantage is taken of the insolubility of the cæσιο-platinic chloride, which is little more than half as soluble in boiling water as the corresponding salt of rubidium. The mixture which contains the rubidium and cæsium is freed from compounds of the earths and other metals by the ordinary methods, and the residue, which

contains salts of the alkalies only, is mixed with a solution of platinic chloride, which if added in excess precipitates nearly the whole of the rubidium and cæsium, together with a large proportion of potassium. By continued boilings of the precipitate with small quantities of water, repeated eighteen or twenty times in succession, so long as the washings have a yellow colour, the potassium salt is removed. The platinum salt is reduced by heating it in a current of hydrogen. The mixed rubidic and cæsic chlorides are dissolved out by water, and converted into sulphates by heating them with an excess of sulphuric acid, which is expelled by ignition. On adding pure baryta water to the solution of the sulphates, the alkalies are obtained in the caustic state, and may then easily be converted into carbonates, either by carbonic acid or ammoniac carbonate. Once more the solution of the mixed carbonates is evaporated to complete dryness, and treated with boiling absolute alcohol, which dissolves out cæsic carbonate, and leaves the rubidic carbonate. On evaporation of the alcoholic solution a tolerably pure cæsic carbonate is obtained.

The best plan of separating cæsium from rubidium, according to Allen and Johnson, consists in taking advantage of the inferior solubility of the hydro-rubidic tartrate ( $\text{RbHC}_4\text{H}_4\text{O}_6$ ). The mixed carbonates are to be neutralized with tartaric acid, and then a quantity of the acid is added equal to that required for converting the rubidium into the acid tartrate, leaving the cæsium in the solution as normal tartrate, which is deliquescent. The solution is concentrated by evaporation until it is nearly saturated at the boiling-point. The rubidium salt crystallizes out on cooling, and may be purified by recrystallization. This acid tartrate ( $\text{RbHC}_4\text{H}_4\text{O}_6$ ) requires 8.5 parts of boiling and 94 parts of water at  $77^\circ$  ( $25^\circ \text{C.}$ ) for its solution. The acid cæsium salt is soluble in its own weight of boiling water, and in 10 parts of water at  $77^\circ$  ( $25^\circ \text{C.}$ ), and the normal salt is deliquescent. (Bunsen, *Pogg. Annal.* cxix. 1.)

An amalgam of cæsium may be procured by submitting a solution of the chloride to electrolysis, employing a globule of mercury for the negative electrode. This amalgam is even more electropositive than that of rubidium, so that cæsium is the most electropositive element as yet discovered.

(609) *Cæsia* ( $\text{Cs}_2\text{O}$ ).—Cæsium appears to form two oxides: a blue suboxide, and a powerfully basic oxide corresponding to potash and soda, termed *cæsia*. *Cæsic hydrate* ( $\text{CsHO} = 150$ ) is very deliquescent, and powerfully caustic: it is readily soluble in alcohol. When heated, it fuses readily, and attacks platinum.

*Cæsic chloride* ( $\text{CsCl} = 168.5$ ) crystallizes in cubes, and is deliquescent: it melts at a low red heat. 100 parts of cæsic chloride contain 21.07 parts of chlorine, while an equal weight of rubidic chloride contains 29.7, and of potassic chloride 47.5 of chlorine.

*Cæsioplatinic chloride* ( $2\text{CsCl}, \text{PtCl}_4 = 676$ ) crystallizes in yellow

transparent octohedra: 100 parts of boiling water dissolve 0.377 of the salt (Bunsen).

*Cæsic sulphate* ( $\text{Cs}_2\text{SO}_4$ ) is anhydrous, permanent in the air, but very soluble in water. It forms double salts with magnesian sulphate, and other sulphates of that class, of the form  $(\text{MgSO}_4, \text{Cs}_2\text{SO}_4 \cdot 6\text{H}_2\text{O})$ . It also yields a crystallizable alum. A *hydrocæsic*, or acid sulphate ( $\text{CsHSO}_4$ ) may be obtained in short rhombic prisms.

*Cæsic nitrate* ( $\text{CaNO}_3 = 195$ ) is anhydrous, and isomorphous with rubidium and potassic nitrates. It is permanent in the air, has a cooling taste, and is soluble in ten times its weight of cold water.

*Cæsic carbonate*, or *Carbonate of cæsium* ( $\text{Cs}_2\text{CO}_3 = 326$ ) is deliquescent: it requires five times its weight of boiling alcohol for solution. *Hydrocæsic carbonate*, or *acid carbonate* ( $\text{CsHCO}_3 = 194$ ) may be obtained in brilliant prismatic crystals, which are permanent in the air.

The salts of cæsium are not easily distinguished from those of potassium and rubidium, except by the characteristic lines in the spectrum of their flame (Part I. p. 180).

#### § VI. AMMONIUM: $\text{H}_4\text{N} = 18$ (*hypothetical*).

(610) *Action of Oxyacid Anhydrides on Ammonia*.—When dry gaseous ammonia ( $\text{H}_3\text{N}$ ) is presented to the anhydrides of the oxyacids, such as sulphuric ( $\text{SO}_3$ ), sulphurous ( $\text{SO}_2$ ), or carbonic ( $\text{CO}_2$ ) anhydride, the gas enters into combination with the anhydride, and a peculiar compound is formed, in which it is maintained by Laurent and Gerhardt that one-half of the ammonia only exists in the form of an ordinary ammoniacal salt, the other half having entered into combination with the elements of the anhydride, to form a compound termed an amidated acid; the product obtained differs, therefore, in many important particulars from the compound which would be obtained by neutralizing with ammonia a solution of the same acid in water. In the latter case one of the ordinary 'salts of ammonia,' as they are usually termed, is produced; in the former case an ammoniacal salt of new amidated acid would be the result; but the preparation of these amidated compounds is difficult, and their true nature is not as yet thoroughly ascertained.\*

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\* These compounds of ammonia with the anhydrides are often incorrectly spoken of as *amides*. The amides of monobasic acids are, properly speaking, salts of ammonium which have been deprived of 1 atom of water. Ammonic benzoate ( $\text{H}_4\text{NC}_6\text{H}_5$ ), for example, when deprived of  $\text{H}_2\text{O}$ , furnishes a white fusible volatile solid known as *benzamide* ( $\text{H}_3\text{NC}_6\text{H}_5\text{O}$ ). The amides of the dibasic acids are ammonium salts which have been deprived of 2 atoms of water. *Sulphamide* would be  $(\text{H}_2\text{N})_2\text{SO}_2$ , and would contain an atom of water less than

The general properties of these bodies may be illustrated by examining the several combinations formed between the sulphuric and sulphurous anhydrides and dry ammoniacal gas.

(611) *Sulphuric ammonide, Sulphat-ammon*  $(\text{H}_3\text{N})_2\text{SO}_3$ .—At least three distinct compounds may be obtained by the action of dry ammonia on sulphuric anhydride. When a current of dry ammoniacal gas is transmitted over sulphuric anhydride, placed in a flask, and maintained at a low temperature, taking care to leave the anhydride somewhat in excess, a hard gummy mass is produced, which when exposed to the air absorbs moisture and gradually deliquesces. The liquid thus obtained is saturated with baric carbonate, in order to remove the excess of acid, and is then evaporated; it yields large transparent crystals derived from an octohedron with a square base. This compound is the *parasulphat-ammon* of Rose, and consists, according to this chemist, of  $(\text{H}_3\text{N})_2\text{SO}_3$ . It is freely soluble in water, but insoluble in alcohol. Its solution has a bitter taste, and gives no precipitate with barium salts, and none with platinic chloride. By long boiling with water, or with a solution of tartaric acid, it is slowly changed into ordinary ammonic sulphate; but if heated with a free alkali, sulphate of the alkali-metal is speedily produced, and ammonia is expelled.

If ammoniacal gas in excess be made to act upon sulphuric anhydride, another compound, isomeric with the former, termed *sulphat-ammon* by Rose, is obtained. It does not crystallize, and is quickly transformed when in solution into ammonic sulphate.

A third compound, which may be procured in beautiful transparent crystals, is prepared by transmitting the vapour of sulphuric anhydride into ammoniacal gas in excess; the solid compound thus obtained is fused in a current of dry ammonia, and dissolved in water. The crystals obtained on evaporation, according to Jacquelin, consist of  $(\text{H}_3\text{N})_2\text{SO}_3$ . Although the solution of this compound has an acid reaction, it gives no precipitate with salts of barium.

(612) *Sulphit-Ammon, or Sulphurous Ammonide*  $(\text{H}_3\text{N})_2\text{SO}_2$ .—If dry gaseous sulphurous anhydride be mixed with an excess of perfectly dry ammoniacal gas, 1 volume of the anhydride and 2 of ammonia combine, and form a yellow amorphous, volatile, deliquescent compound, which, when dissolved in water, undergoes gradual decomposition (Rose).

If the sulphurous anhydride be in excess, a different compound is formed  $(\text{H}_2\text{NSO}_2)$ , corresponding in composition to hydro-ammonic sulphite from which 1 atom of water has been abstracted:  $\text{H}_2\text{NSO}_2 = \text{H}_4\text{NHSO}_3 - \text{H}_2\text{O}$ . It is a

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sulphuric ammonide. The *ammonides*, or *ammons*, as these compounds of ammonia with the anhydrides of dibasic acids have been termed, contain only one atom of water less than the ordinary ammonium salts. Ammonic sulphate, for instance, may be represented as  $(\text{H}_3\text{N})_2\text{SO}_4$ , while sulphuric ammonide contains  $(\text{H}_3\text{N})_2\text{SO}_3$ , or  $\text{H}_3\text{N} \cdot \text{SH} \cdot \text{NO}_3$ . The different varieties of compounds obtained from the salts of ammonia by dehydration will be considered amongst the products of organic chemistry.

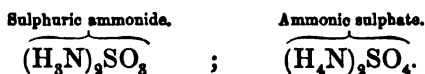
reddish-yellow, crystalline, volatile substance, freely soluble in water: when in solution, it is speedily decomposed into ammoniac sulphate and trithionate;  $4(\text{H}_4\text{NSO}_3) + 2\text{H}_2\text{O} = (\text{H}_4\text{N})_2\text{SO}_4 + (\text{H}_4\text{N})_2\text{S}_3\text{O}_6$ . No such decomposition occurs when the ordinary hydro-ammoniac sulphite is dissolved in water.

Phosphoric and carbonic anhydrides also form ammonides, which are analogous to those just described.

(613) *Action of Anhydrous Hydracids on ammonia.*—Dry ammoniacal gas likewise unites with facility with the anhydrous hydracids; the compounds which are thus produced do not correspond in properties to the ammonides, but, on the contrary, form ordinary ammonium salts. For example, dry hydrochloric acid and dry ammoniacal gases unite with avidity, and a white solid compound is produced, which is ordinary sal ammoniac; when dissolved in water it gives with solution of argentic nitrate the usual curdy precipitate indicative of chlorine, and with platinic chloride the usual yellow double salt characteristic of ammonium salts is deposited.

(614) *Theory of Ammonium.*—The differences between the characters of the compounds which dry ammonia forms with the oxyacid anhydrides, and those which it produces with the anhydrous hydracids were explained by Berzelius with the aid of a hypothesis originally suggested by Ampère, which has been termed 'the ammonium theory,' by the adoption of which the salts of ammonia admit of being considered as possessing a constitution analogous to that of the metallic salts.

According to this view, the compounds which are frequently spoken of as salts of ammonia with the oxyacids do not contain ammonia at all, but a compound in which the elements of an atom of water have been added to those of ammonia [ $\text{H}_3\text{N} + \text{H}_2\text{O}$ ]: in consequence of the assimilation of this atom of water, the substance which is formed may be regarded as  $(\text{H}_4\text{N})\text{HO}$ , ammoniac hydrate, analogous to potassic hydrate ( $\text{KHO}$ ), and the basyl of the salts which it yields would be the compound body ammonium ( $\text{H}_4\text{N}$ ), which takes the place of a metal. Anhydrous ammonia, when it unites with the oxyacid anhydrides, must therefore produce bodies very different from those obtained by the combination of hydrated ammonia with the compounds formed by the action of the same anhydrides upon water, as may be seen, for instance, by comparing the formula of the compound of ammonia with sulphuric anhydride, and with sulphuric acid when water is present:—



It is likewise easy to see why, by the combination of anhydrous

ammonia with a hydracid equally free from water, a true ammonium salt should be formed: for instance, hydrochloric acid and ammonia by their union yield ammonic chloride, a salt which obviously presents the closest analogy with the metallic chlorides;  $H_3N + HCl = (H_4N)Cl$ .

With the oxyacids, then, on the one hand, and with their anhydrides on the other, ammonia forms two distinct classes of compounds; the more important class constitutes the normal salts of the alkali in which the elements of water are necessarily present; the other class consists of the ammonides already described.

The theory of ammonium is supposed to derive considerable support from the following remarkable experiment:—If an amalgam of potassium or of sodium be moistened with a concentrated solution of sal ammoniac ( $H_4NCl$ ), the amalgam immediately begins to increase in bulk, and ultimately swells up till it acquires 8 or 10 times its original volume, and it at the same assumes a pasty consistence, but still preserves its metallic lustre. This substance, if exposed to a temperature of  $0^\circ$  ( $-18^\circ C.$ ), crystallizes in cubes. It begins to undergo spontaneous decomposition immediately after its production, and the same effect occurs still more rapidly if it be placed in water: hydrogen gas is given off in minute bubbles, and ammonia is found in the solution. It is generally supposed that this remarkable amalgam consists of a combination of  $H_4N$  (or ammonium) with mercury. On attempting to expel the mercury by heat, however, the compound is decomposed, metallic mercury is sublimed, and a mixture of hydrogen and ammoniacal gas evolved: all other attempts to isolate the ammonium have been equally unsuccessful. The proportion of ammonium present in the amalgam, notwithstanding the great change in bulk and in properties experienced by the mercury, is extremely minute, amounting, according to Gay-Lussac and Thénard, to little more than one two-thousandth of the weight of the mercury.

(615) *Solution of Ammonia*.—The preparation of ammoniacal gas and of its aqueous solution have been already described (369, 370). The solution in water has an intensely alkaline reaction, and may be regarded as a solution of ammonic hydrate ( $H_4NHO$ ); but when heated, pure ammoniacal gas ( $H_3N$ ) alone is expelled, and by passing the gas through a tube filled with quicklime, to absorb the water which it carries over with it in suspension, ammonia may be obtained in a state of purity. The solution in water, when neutralized by acids and evaporated, yields the ordinary ammonium salts.

The compounds of ammonium are continually receiving fresh applications. The sulphate and the chloride are extensively used in the preparation of ammonium-alum, as a substitute for the corresponding compounds of potassium; for agricultural purposes the sulphate is largely used, as a manure for cereal crops. Caustic ammonia is employed by the dyer as a solvent for cochineal; it is essential in the preparation of orchil and the lichen colours. A remarkable application of ammonia has also lately been made in Carré's refrigerating machines (*note*, Part I. p. 339), which are already extensively used in chemical operations on a large scale.

(616) **SULPHIDES OF AMMONIUM.**—Ammonium forms several sulphides which are freely soluble in water. *Diammonic sulphide*, or the *protosulphide*  $[(H_4N)_2S]$ , cannot be procured in a solid form: it may be prepared in solution by dividing a quantity of solution of ammonia into two equal portions, through one of which sulphuretted hydrogen is transmitted so long as it is absorbed; the saturated liquid is then added to the second portion of the solution. It is, however, possible, though not probable, that the two solutions  $H_4N, HS$  and  $H_4N, HO$  may remain uncombined, instead of uniting to form  $(H_4N)_2S + H_2O$ . This liquid dissolves many of the sulphides of the metals which furnish acids with oxygen, and forms double sulphides with them (535, 551). Many of these double sulphides may be obtained in crystals; this, for example, is the case with those which contain the diantimonic and diarsenic pentasulphide, and the molybdic trisulphide.

*Diammonic disulphide*  $(H_4N)_2S_2$  may be obtained in large yellow, transparent, very deliquescent crystals, by passing sulphur vapour and dry ammonia through a red-hot porcelain tube. In the hydrated form it has been long known as *Boyle's fuming liquor*, and is prepared by calcining 3 parts of slaked lime with 2 of sulphur, and distilling 3 parts of this mixture with 2 of sal ammoniac and 1 part of sulphur: a yellow, oily, fetid liquor, which fumes in the air, passes over, and on cooling it deposits deliquescent yellow lamellar crystals; acids disengage hydrosulphuric acid from it, and cause a deposit of sulphur. Its aqueous solution dissolves a large quantity of sulphur, forming a *pentasulphide*  $(H_4N)_2S_5$ , which crystallizes from its solution in long orange-yellow oblique rhombic prisms. Fritsche has also obtained a crystallized compound containing  $(H_4N)_2S_7$ .

*Ammonio-hydric sulphide*, or *Sulphhydrate of ammonium*  $(H_4NHS=51)$  is the liquid commonly used as a reagent under the name of hydrosulphate of ammonia: it is formed by transmitting sulphuretted hydrogen through a solution of ammonia to saturation. This liquid, when newly prepared, is colourless, but it absorbs oxygen rapidly from the air, and becomes yellow from formation of ammonic disulphide, whilst ammonic hyposulphite is produced in the liquid;  $8H_4NHS + 5O_2 = 2[(H_4N)_2S_2] +$



$2[(\text{H}_4\text{N})_3\text{S}_2\text{H}_2\text{O}_4] + 2\text{H}_2\text{O}$ . A solution of ammonic hydro-sulphide dissolves the sulphides of the electronegative metals as readily as diammonic sulphide does, but sulphuretted hydrogen is liberated: for example,  $6\text{H}_4\text{NHS} + \text{As}_2\text{S}_3 = 2[(\text{H}_4\text{N})_3\text{AsS}_4] + 3\text{H}_2\text{S}$ . Ammonio-hydric sulphide may be obtained in the anhydrous form, by mixing dry sulphuretted hydrogen with dry ammoniacal gas; 2 volumes of ammonia combine with 2 of sulphuretted hydrogen, and condense in yellowish, transparent, brilliant plates, which are very volatile, and sublime without decomposition; they are very soluble in water.

(617) AMMONIC CHLORIDE, or *Chloride of ammonium* ( $\text{H}_4\text{NCl}$  = 53.5); *Sp. Gr. of Solid*, 1.578; *of Vapour*, 0.89; *Mol. Vol. of Vapour*,  ;\* *Comp. in 100 parts*, HCl, 68.22;  $\text{H}_3\text{N}$ ,

31.78.—*Muriate of Ammonia*, or *Sal Ammoniac* as it is commonly termed, is the most important of the salts of ammonium. It may be formed directly by the union of hydrochloric acid and ammoniacal gases: it was formerly imported from Egypt in considerable quantity as a product of the distillation of dried camel's dung, but in this country it is now furnished almost entirely from *ammoniacal liquor*, a waste product from the coal-gas works. Coal contains a portion of nitrogen, which, during the process of distillation, is partially converted into ammonia; this combines with carbonic acid and with sulphuretted hydrogen: these compounds are condensed with the gas liquor, from which the ammonia is subsequently extracted. The best process for preparing sal ammoniac consists in neutralizing the gas liquor with hydrochloric acid. For this purpose the liquid is pumped up from a tank into the decomposer—a large wooden vat closely fitted with a cover, connected with flues for carrying off the gaseous products; the acid in suitable quantity is placed in jars, from which it is drawn off slowly by siphons, and is thus allowed to mix gradually with the liquor; abundance of gas is disengaged, and is made to pass through a fire, where the sulphuretted hydrogen is burned; much of the tarry matter (derived from the coal) which was held in solution, is deposited during this operation, and the liquid froths up considerably, any loss which might be thus occasioned being prevented by the use of a waste-pipe, by which the overflow is carried back into the tank below. When the

\* The vapour-volume of this and of several ammonium salts, including the bromide and cyanide, is anomalous, being double that of most compounds. Many chemists consider that in the act of evaporation these compounds are separated into the free hydracid and free ammonia (Part I. *note*, p. 103).

liquor has thus been neutralized, it is run into a covered evaporating pan, where the remaining portions of sulphuretted hydrogen are expelled; after further concentration it is drawn off into shallow wooden vessels, lined with lead, to crystallize: the crystals thus procured are drained, and the mother-liquor is again concentrated. The rough crystals are next heated in a cast-iron pan, to a point approaching that at which sublimation commences; a good deal of tarry matter, which the salt still retains, is expelled during this roasting. The salt is then sublimed in a strong cylindrical iron pot, furnished with a leaden or iron cover lined with fire-clay; the fire underneath is gradually raised, and the salt sublimes and is deposited in a large dome-shaped cake on the inner surface of the cover.

The liquors which are condensed during the distillation of bones in closed iron cylinders, in the process of preparing animal charcoal, are highly charged with an impure carbonate of ammonium, contaminated with volatile oily and tarry products derived from the action of heat upon animal matter; these liquors furnish a source of ammoniacal salts of some importance: formerly this liquid, after being subjected to a partial purification, was commonly known as *spirit of hart's-horn*, because a similar liquor was originally obtained by the distillation of horn shavings.

Sublimed ammonic chloride forms semi-transparent, tough, fibrous masses. It is very soluble in water, 100 parts of which at  $59^{\circ}$  ( $15^{\circ}$  C.) dissolve 36 parts, and at the boiling-point, 88.9 parts of the salt: a great reduction of temperature occurs whilst it is undergoing solution, and it is hence employed as a common ingredient in freezing mixtures; it crystallizes usually in an arborescent form, but sometimes in cubes and octohedra. Sal ammoniac has a sharp, acrid taste; it is slightly soluble in alcohol. When heated, it sublimes much below redness, before undergoing fusion. It has a strong tendency to form double salts with the chlorides more electronegative than itself. The compounds of many metals which form volatile chlorides, such as the arseniates and arsenites, the antimonates and the stannates, when heated with ammonic chloride, lose the arsenic, antimony, and tin in the form of chlorides of these metals; and the salts of lead, iron, zinc, and aluminum, are decomposed and completely volatilized when ignited with a large excess of sal ammoniac. Rose observed that all the basic protoxides of the form  $N^{\prime\prime}O$ , such as protoxides of iron, cobalt, and manganese—and oxides of the form  $N_2O$ , such as suboxide of copper, also decompose ammonic chloride, when heated with its solution, the ammonia being displaced

by the metallic oxide, and a fixed metallic chloride being formed, whilst not one of the sesquioxides has this power.

*Ammonic iodide* ( $H_4NI$ ).—This is a salt which crystallizes in cubes: it is used to some extent by the photographer, and may be obtained by decomposing calcic iodide by the addition of ammonia and ammoniacal sesquicarbonate in slight excess; the solution filtered from the precipitated calcic carbonate yields pure ammoniacal iodide.

(618) **AMMONIC SULPHATE**, or *Sulphate of ammonium* [ $(H_4N)_2SO_4 = 132$ ; *Sp. Gr.* 1.695] is prepared in large quantity by subjecting gas liquor to distillation, and condensing the volatilized ammonia in sulphuric acid. The salt crystallizes out from the strongly acid liquor, which is employed to condense fresh ammonia in subsequent operations. On a small scale it may be obtained in a pure form by adding ammoniacal sesquicarbonate to dilute sulphuric acid so long as any effervescence ensues. It crystallizes in flattened prisms, which are isomorphous with those of potassic sulphate: it is soluble in twice its weight of cold water, and has a sharp disagreeable taste; when heated it decrepitates; at  $284^\circ$  ( $140^\circ$  C.) it melts, and between  $500^\circ$  and  $599^\circ$  ( $260^\circ$  and  $315^\circ$  C.) it undergoes partial decomposition, ammoniacal sulphite being among the products. It forms a great number of double salts isomorphous with the corresponding potassium salts. Ammonic sulphate has lately been applied to muslins and other fabrics for the purpose of preventing them from burning with flame in case they should accidentally take fire. The finished goods are dipped into a solution containing 10 per cent. of the salt, and dried in a centrifugal machine, or *hydro-extractor*.

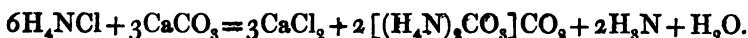
A *hydro-ammonic sulphate*, or *acid sulphate* may be formed which has the formula [ $(H_4N)_3H_2SO_4$ ]; and a *sodio-ammonic sulphate* ( $H_4NNaSO_4 \cdot 2H_2O$ ) may be readily formed by mixing solutions of sodic and ammoniacal sulphates in equivalent proportions, and evaporating the liquid till it begins to crystallize.

(619) **AMMONIC NITRATE**, or *Nitrate of ammonium* ( $H_4NNO_3 = 80$ ); *Sp. Gr.* 1.635.—This is a salt of some importance to the chemist, as it furnishes him with a ready source of pure nitrous oxide. It is procured by neutralizing nitric acid with a solution of ammoniacal sesquicarbonate: on evaporation, the salt crystallizes in long striated anhydrous prisms; by rapid evaporation it is obtained either in a fibrous or in an amorphous mass. It has a bitter acid taste, is somewhat deliquescent, and during the act of solution causes a great depression of temperature, hence it is often used in frigorific mixtures: when heated to  $226^\circ$  ( $107^\circ.8$  C.) it melts, and at  $482^\circ$  ( $250^\circ$  C.) it undergoes complete decomposition, being converted into nitrous oxide and water, in the

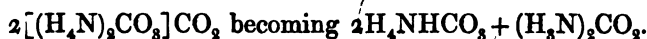
manner already described (364);  $\text{H}_4\text{NNO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$ . If thrown on a red-hot plate it melts, hisses, and is dispersed with a faint bluish flame.

(620) CARBONATES OF AMMONIUM.—Normal ammonic carbonate  $[(\text{H}_4\text{N})_2\text{CO}_3]$  is not known in the solid form, though it may exist in solution. When carbonic anhydride and dry ammonia are mixed, no matter in what proportions, 2 volumes of ammonia and 1 of carbonic anhydride unite, and are condensed into a white solid, ammonic carbamate being formed: according to Gerhardt,  $2\text{H}_3\text{N} + \text{CO}_2 = \text{H}_4\text{NH}_2\text{NCO}_2$ . This compound is rapidly converted by water into normal ammonic carbonate:  $\text{H}_4\text{NH}_2\text{NCO}_2 + \text{H}_2\text{O} = (\text{H}_4\text{N})_2\text{CO}_3$ . There are, however, several compounds of ammonium with carbonic acid.

The most important of these is the so-called *sesquicarbonate*, the common carbonate or *smelling-salts* of the shops  $2[(\text{H}_4\text{N})_2\text{CO}_3]\text{CO}_2 = 236$ , or  $2(\text{H}_4\text{N})_2\text{O}_3\cdot 3\text{CO}_2$ ; *Comp. in 100 parts*,  $\text{H}_2\text{N}$ , 28·81;  $\text{CO}_2$ , 55·93;  $\text{H}_2\text{O}$ , 15·26. It is usually obtained as a semi-transparent fibrous mass, by mixing chalk with half its weight of sulphate, or of chloride of ammonium, collecting in leaden vessels the crude product which comes over on applying heat, and resubliming the mixture at a temperature of about  $149^\circ$  ( $65^\circ \text{C.}$ ); the salt is received in leaden hoods, in the interior of which it is deposited. During this process a large quantity of free ammonia escapes, because the normal carbonate cannot exist at that temperature. The decomposition of the ammonic chloride may be represented thus:—



Ammonic sesquicarbonate has a strong, pungent smell, like that of pure ammonia, arising from the continual volatilization of carbonic ammonide at ordinary temperatures:



Owing to this loss of ammonia the salt speedily becomes coated with a white spongy crust of bicarbonate. If the powdered salt be placed upon a filter, and washed with successive small quantities of cold water, the normal carbonate may be gradually dissolved away, and the salt known as the bicarbonate, which is a more sparingly soluble salt, will be left upon the filter. The sesquicarbonate has an acrid taste and a strongly alkaline reaction. In its ordinary form the sublimed salt has a composition which is exceptional, since in order to convert it into a normal sesquicarbonate it would require an additional atom of water, which is never found in the commercial salt; but its aqueous solution, if saturated and ex-

posed to a temperature of  $32^{\circ}$  ( $0^{\circ}$  C.), deposits large, transparent octohedra with a rhombic base, of the hydrated true sesquicarbonate  $[(\text{H}_4\text{N})_4\text{H}_2\text{CO}_3, 2\text{H}_2\text{O}]$ . According to the researches of Rose there are several compounds resulting from the combination of the carbonate with different proportions of bicarbonate of ammonium.

*Hydro-Ammonic Carbonate, or Bicarbonate of Ammonium* ( $\text{H}_4\text{NHCO}_3 = 79$ ; *Sp. Gr.* 1.586) is isomorphous with the corresponding potassium salt: it is soluble in 8 parts of cold water, and if the solution be heated, carbonic acid escapes; when exposed to the air the dry salt becomes slowly volatilized. It may be obtained in large transparent prismatic crystals, derived from a rhombic octohedron  $[4\text{H}_4\text{NHCO}_3, \text{H}_2\text{O}]$ , by pouring boiling water upon the sesquicarbonate, corking the flask, and allowing it to cool. It is sometimes formed spontaneously during the decomposition of guano, and is then deposited in large regularly formed crystals.

Ammonic carbonate combines with many metallic carbonates, forming double salts.

(621) **PHOSPHATES OF AMMONIUM**, corresponding to those of sodium may be formed; but the only one of any importance is the sodio-ammonio-hydric phosphate, known as *microcosmic salt* ( $\text{Na}, \text{H}_4\text{N}, \text{H}, \text{PO}_4, 4\text{H}_2\text{O} = 137 + 72$ ). It is prepared by mixing a hot solution of 6 parts of hydro-disodic phosphate with a solution of 1 part of ammonic chloride in the smallest possible quantity of water; common salt remains in solution, and the phosphate crystallizes in large transparent prisms, which are efflorescent in a dry air. It may be purified by a second crystallization from a small quantity of hot water to which a little free ammonia has been added, to compensate for the loss of ammonia which the salt sustains when heated in solution. By ignition, all the ammonia and water are expelled, sodic metaphosphate remains, and fuses into a colourless glass at a red heat. This salt is sometimes employed as a flux for experiments with the blowpipe, as the glass dissolves many metallic oxides, and forms transparent beads, from the colour of which the presence of certain metals can in many cases be ascertained.

(622) *Ammoniated Salts*.—Anhydrous ammonia enters into combination with many anhydrous metallic salts in a manner somewhat analogous to that of water of crystallization. In other cases, salts which usually retain water of crystallization lose it either partially or entirely when they combine with ammonia, but the number of atoms of ammonia is not influenced by the pro-

portion of water with which the salt generally unites. Chloride of silver, of tin, of copper, and of calcium, sulphate of copper, and of zinc, nitrate of silver, and of copper, form compounds of this kind with ammonia. The composition of some of these salts is exhibited in the subjoined table:—

				At. wt.	Sp. gr.
Ammoniated argentic chloride	...	$\text{AgCl}_2\cdot 2\text{H}_3\text{N}$	...	177.5	
1. " cupric "	...	$\text{CuCl}_2\cdot 6\text{H}_3\text{N}$	...	236.4	
2. " " "	...	$\text{CuCl}_2\cdot 4\text{H}_3\text{N}\cdot \text{H}_2\text{O}$	...	220.4	1.671
3. " " "	...	$\text{CuCl}_2\cdot 2\text{H}_3\text{N}$	...	168.4	2.194
" calcic "	...	$\text{CaCl}_2\cdot 8\text{H}_3\text{N}$	...	247	
" argentic sulphate	...	$\text{Ag}_2\text{SO}_4\cdot 4\text{H}_3\text{N}$	...	380	2.918
" cupric "	...	$\text{CuSO}_4\cdot 4\text{H}_3\text{N}\cdot \text{H}_2\text{O}$	...	245.4	1.790
" argentic nitrate	...	$\text{AgNO}_3\cdot 3\text{H}_3\text{N}$	...	221	
" cupric "	...	$\text{Cu}_2\text{NO}_3\cdot 4\text{H}_3\text{N}$	...	255.0	1.874

These compounds when exposed to the air lose a portion of the ammonia: if heat be applied, the ammonia is often entirely expelled, as in the case of ammoniated argentic chloride, the compound originally employed by Faraday for obtaining ammoniacal gas in the liquid form: the argentic chloride is left unaltered when the ammonia is driven off. In other instances the elements of ammonia react upon the salt and decompose it. For example, ammoniated cupric chloride,  $\text{CuCl}_2\cdot 6\text{H}_3\text{N}$ , when heated, first loses 4 atoms of ammonia, and then the residue ( $\text{CuCl}_2\cdot 2\text{H}_3\text{N}$ ) undergoes the following decomposition;  $6(\text{CuCl}_2\cdot 2\text{H}_3\text{N}) = 6\text{CuCl} + 6\text{H}_4\text{NCl} + 4\text{H}_3\text{N} + \text{N}_2$ . The corresponding nickel compound is reduced to the metallic state when heated.

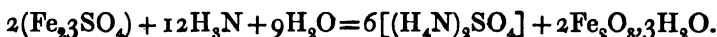
In solution ammonia also combines with many metallic salts, forming analogous compounds: by exposure to air the ammonia escapes. Zinc salts form a colourless solution with excess of ammonia; those of cobalt give a brown, which passes into red; while both nickel and copper salts give a violet-blue solution.

(623) *Action of Ammonia upon Salts in Solution.*—From what has been already stated, it is evident that ammonia acts upon metallic salts not merely as a powerful base, as in cases where caustic potash or soda are made to decompose them. The results produced by the addition of ammonia to a solution of a metallic salt may be stated as follows:—

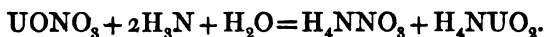
1.—If the ammonia be insufficient in quantity to neutralize the whole of the acid contained in the metallic salt, a sparingly soluble basic salt of the metal may be precipitated: in this way basic cupric sulphate, basic plumbic nitrate, or basic aluminic sulphate may be formed; for instance,  $4\text{CuSO}_4 + 6\text{H}_3\text{N} + 7\text{H}_2\text{O} = 3[(\text{H}_4\text{N})_2\text{SO}_4] + (\text{CuSO}_4)_3\text{CuO}\cdot 4\text{H}_2\text{O}$ .

2.—If the ammonia be present in excess, it may, by reacting

upon the acid of the salt, produce with it a soluble ammonium salt, whilst a precipitate of the metallic oxide in a hydrated form is occasioned: as when alumina, chromic oxide, or ferric oxide, is thrown down from its salts:—for example,



3.—Sometimes the ammonia, if in excess, combines with the precipitated oxide, as it does with uranic oxide, when mixed with a solution of uranic nitrate:—



4.—In other cases a double salt of ammonium and the metal may be precipitated, as when ammonia is mixed with a solution containing phosphoric acid and magnesium, in which case an ammonio-magnesian phosphate is formed and deposited in crystals, which contain water not shown in the equation:  $\text{MgSO}_4 + (\text{H}_4\text{N})_3\text{PO}_4 = (\text{H}_4\text{N})_2\text{SO}_4 + \text{H}_4\text{NMgPO}_4.$

Reactions corresponding to the four modes of action just indicated frequently occur, when a solution of a caustic alkali, such as potash or soda, is mixed with a metallic salt in solution.

5.—A soluble compound may be formed, into the composition of which both the metallic oxide and the ammonia enter, and unite with the acid so as to form a species of double basic salt. Magnesian hydrate, hydrated oxide of copper, of zinc, of cobalt, or of nickel, when free from acid, is very sparingly dissolved by a solution of pure caustic ammonia, but a mixture of ammoniac chloride, or even of ammoniac carbonate with caustic ammonia, dissolves them without difficulty. The compounds thus dissolved are definite in composition, and similar in nature to those enumerated in the table given in the preceding page as the result of the action of ammoniacal gas upon the dry salts of the metals. The solutions of these salts in ammonia frequently absorb oxygen rapidly if exposed to the air: salts of iron, manganese, and cobalt furnish examples of this kind.

6.—But it occasionally happens that the elements of ammonia enter into the composition of the salt in a more intimate manner. When a solution of corrosive sublimate ( $\text{HgCl}_2$ ) is mixed with a solution of potash, a yellow precipitate of mercuric oxide is formed, and potassic chloride remains in solution;  $\text{HgCl}_2 + 2\text{KHO} = \text{HgO} + 2\text{KCl} + \text{H}_2\text{O}$ ; but the case is otherwise if ammonia be used instead of potash; a white precipitate is then formed, the composition of which is unchanged by the addition of an excess of ammonia. Kane (*Phil. Mag.*, June, 1836, p. 495) showed that this body has a composition which may be represented

by the formula of  $\text{HgCl}_2\text{HgH}_4\text{N}_2$ . Its formation may be explained by the following equation :—



From this result, conjoined with others obtained from an examination of other ammoniacal derivatives from copper, palladium, and other metals, Kane was led to believe that ammonia is not a direct compound of hydrogen with nitrogen, but rather a combination of an atom of amidogen with one of hydrogen; so that he represents ammonia as  $\text{HAd}$  ( $\text{Ad}$  standing for amidogen,  $\text{H}_2\text{N}$ ); the atom of hydrogen being liable to displacement by an equivalent either of mercury or of certain other metals. One atom of such an amide of mercury ( $\text{HgAd}_2$ ) is, according to Kane, contained in white precipitate, in combination with 1 atom of mercuric chloride.

Later experiments, however, especially those of Hofmann, on the formation of bases by substitution from ammonia, have not strengthened the theory proposed by Kane; they have shown that not only does 1 atom of hydrogen admit of being displaced by some equivalent substance, but that each of the 3 atoms of hydrogen in ammonia admits of being thus displaced; nay more, that bodies may be obtained which are derived from ammonium, in which all the 4 atoms of hydrogen in this compound have been displaced by other equivalent bodies. These investigations point rather to the view that white precipitate is a body corresponding in composition to ammoniac chloride ( $\text{H}_4\text{N}_2\text{Cl}$ ) but in which 2 atoms of hydrogen are displaced by 1 atom of the dyad metal mercury ( $\text{Hg}''\text{H}_2\text{N}_2\text{Cl}$ ). We shall recur to these investigations when considering the properties of the organic bases.

7.—Within the last few years several remarkable bases which are derived from ammonia have been formed, but into the composition of which certain metals enter. Although these compounds contain the elements of ammonia, and of the oxides of the metals, yet they do not, by means of the ordinary tests, give any indications either of ammonia or of the metals which enter into their composition.

In this manner several series of compounds have been procured, some of which contain platinum, others contain cobalt, and others palladium; in most instances they form crystallizable and well characterized salts.

Amongst the compounds thus formed, four of those obtained from platinum may be selected by way of illustration. The first of these contains a base for which Gerhardt has proposed the



name of *platosamine*,  $\text{PtH}_6\text{N}_3\text{O}$ ; the second, he has termed *diplatosamine*,  $\text{PtH}_{12}\text{N}_4\text{O}$ ,  $\text{H}_2\text{O}$ ; the third, *platinamine*,  $\text{PtH}_6\text{N}_2\text{O}_2$ ,  $2\text{H}_2\text{O}$ ; and the fourth, *diplatinamine*,  $\text{PtH}_{12}\text{N}_4\text{O}_2$ . The base last mentioned has not as yet been obtained in a separate form.

Each of these bases forms with hydrochloric acid a crystallizable salt, the composition of which is represented by the empirical formula given in the second column of the following table, whilst the third column shows the relation of the compound to the chloride of platinum from which it is obtained; the first two compounds being derived from platinous chloride, the last two from platinic chloride:—

Platosamine dichloride	$\text{PtH}_6\text{N}_2\text{Cl}_3$ or $\text{PtCl}_2, 2\text{H}_3\text{N}$ .
Diplatosamine dichloride	$\text{PtH}_{12}\text{N}_4\text{Cl}_2$ „ $\text{PtCl}_2, 4\text{H}_3\text{N}$ .
Platinamine tetrachloride	$\text{PtH}_6\text{N}_2\text{Cl}_4$ „ $\text{PtCl}_4, 2\text{H}_3\text{N}$ .
Diplatinamine tetrachloride	$\text{PtH}_{12}\text{N}_4\text{Cl}_4$ „ $\text{PtCl}_4, 4\text{H}_3\text{N}$ .

(624) CHARACTERS OF THE COMPOUNDS OF AMMONIUM.—The ammonium salts are colourless; they are all decomposed by heat, unless the acid itself be capable of volatilization, in which case they may generally be sublimed without change. They are distinguished from the salts of all the metals, with the exception of those of the alkaline group, by the absence of any precipitate when their solutions are mixed with a solution of potassic or sodic carbonate.

The ammonium salts may be recognized by heating them in the solid form with *quicklime* or with *caustic potash*, when pungent fumes of ammonia are extricated: if their solutions be boiled with either potassic or calcic hydrate a similar extrication of ammonia ensues, and if the quantity of ammonia be too small to be detected by the smell, a rod dipped into *hydrochloric acid* diluted with an equal bulk of water, produces white fumes when brought into the vapour; these fumes are due to the production of sal ammoniac, which is formed by the union of the gaseous ammonia with the vapour of the hydrochloric acid, and is precipitated in the solid form. A characteristic test of free ammonia is the formation of the black iodide of nitrogen in a solution of iodine in potassic iodide; but if the proportion of ammonia be very minute, the only perceptible change is the disappearance of the brown colour of the solution.

Another still more delicate test of the presence of free ammonia is afforded by the use of a liquid consisting of a mixture of equal parts of a saturated solution of arsenious acid and of a solution containing 2 per cent. of argentic nitrate; traces of

ammonia cause the formation of the yellow triargentic arsenite (Dr. A. Taylor). This, however, though a sensitive, is not a characteristic test, since a trace of any free alkali or alkaline earth produces a similar result.

Another very characteristic and extremely delicate test of ammonia and of its salts is the following:—Prepare a solution of corrosive sublimate to which potassic iodide is added until the precipitate of mercuric iodide is nearly redissolved; then pour into the clear liquid a solution of caustic potash, and allow it to become perfectly clear by standing, then decant the liquid. If this solution be added in excess to a liquid containing a trace of ammonia, or of its salts, it assumes a brown tinge, or furnishes a brown precipitate, according as the proportion of ammonia is less or more, hydrarg-ammonium iodide, or ammonium in which 4 atoms of hydrogen are displaced by 2 of mercury ( $\text{Hg}_2'\text{N}_2\text{I}_2\text{H}_2\text{O}$ ) being formed (Nessler). The reaction does not occur in the presence of sulphides or cyanides of the metals of the alkalies. According to Schöyen a still more sensitive reaction, capable of indicating 1 part in 15 millions, may be obtained by adding to about 100 c. c. of water, 1 c. c. of a solution of corrosive sublimate (1 to 30), and the same quantity of a solution of potassic carbonate (1 to 50), the precipitate consisting of  $\text{Hg}_2'\text{NCl}_2\text{H}_2\text{O}$ , or the chlorine compound corresponding to Nessler's iodide.

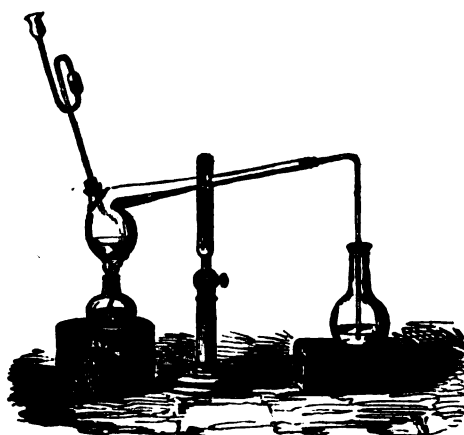
*Sodic Phosphomolybdate* is also a very delicate test for the presence of an ammonium salt in solution. The mode of preparing and applying it is described under the head of molybdic acid (829).

(625) *Estimation of Ammonia*.—The most accurate method of determining the quantity of ammonia in any substance, if the absence of potassium has been ascertained, consists in precipitating it by *platinic chloride*, observing all the precautions mentioned when speaking of the use of this test for potassium (580); a yellow insoluble double salt falls, consisting of  $(2\text{H}_4\text{NCl}_2\text{PtCl}_6)$ ; it contains, in 100 parts, 7.62 of ammonia. This salt is easily distinguished from the corresponding potassium compound by heating it to redness, in which case metallic platinum alone remains; whereas the potassium salt, though decomposed by this treatment, leaves the platinum mixed with potassic chloride, which may be dissolved out of the residue.

(626) The following method of determining the amount of ammonia in guano or in crude ammoniacal salts will often be found useful. Ten grammes of the matter for trial are placed in a small retort, fig. 347, and 100 cub. centim. of water are added: by means of a bent funnel 25 c. c. of a solution of potash, of specific gravity 1.25, is also introduced; 50 or 60 c. c. of liquid is gradually distilled

into the flask, which contains 100 c. c. of sulphuric acid diluted to the strength required for the determination of soda for alkalimetical purposes (577). If the

FIG. 347.



mixture froths up inconveniently when boiled, milk of lime may be substituted for the solution of potash. As soon as 50 or 60 c. c. of liquid has been distilled, the contents of the retort are allowed to cool a little, and 40 c. c. of water is introduced into the retort by the funnel; a second distillation is then proceeded with, until the quantity of water just added has passed over; 40 c. c. more of water is again added to the contents of the retort, and the distillation is renewed a third time until this additional quantity of water has passed over: the liquid in the flask is then mixed with a few drops of infusion of litmus.

This is now to be neutralized in the usual way, by means of a standard solution of caustic soda; the soda solution being of such a strength that one c. c. of it exactly neutralizes an equal measure of the acid liquid originally introduced into the flask. Suppose that this liquid from the flask now requires 67 c. c. of soda solution instead of 100; 33 measures of the acid will have been neutralized by the ammonia; a quantity of ammonia will therefore have passed over equivalent to 3.3 grammes of anhydrous soda. The corresponding quantity of ammonia may be calculated from the equivalent numbers of the two alkalis:—

Thus, 
$$\begin{array}{ccc} \text{Eq. Na}_2\text{O.} & & \text{Eq. H}_2\text{N.} \\ 31 & : & 17 :: 3.3 : 1.809 \end{array}$$

10 grammes of the material operated on in this case would therefore have contained 1.809 grms., or the sample would contain 18.09 per cent. of ammonia.

## CHAPTER XIII.

### GROUP II.—METALS OF THE ALKALINE EARTHS.

Metal.	Symbol.	Atomic weight.	Atomic vol.	Specific gravity.	Electric conductivity. 68—62 F°.
Barium ... ..	Ba	137.0			
Strontium ... ..	Sr	87.5	34.56	2.54	6.71
Calcium ... ..	Ca	40.0	25.28	1.578	22.14

THESE metals furnish but a single basic oxide: this is soluble in water, combining with it with great avidity. The hydrate absorbs

carbonic acid rapidly, forming a white carbonate, insoluble in water. The hydrates also absorb chlorine, forming bleaching compounds. Each metal forms several sulphides. The protosulphide is less soluble than the others, and is colourless, whilst all the others are yellow. The sulphates, phosphates, and oxalates are insoluble, or nearly so (see also p. 329).

§ I. BARIUM: ( $Ba'' = 137.0$ ).

(627) BARIUM occurs abundantly in the form of sulphate, and is not unfrequently found as carbonate. Davy first procured it in the metallic state by making mercury the negative electrode of a voltaic battery in a strong solution of baric hydrate; the barium was thus obtained as an amalgam, from which the mercury was expelled by heating it strongly in a green glass tube filled with hydrogen; but it does not appear to have been thus isolated in a state of purity. When procured by the voltaic decomposition of its fused anhydrous chloride, it is of a pale yellow colour; but it is not easily obtained in distinct beads. Barium decomposes water rapidly at ordinary temperatures. In the air it is quickly tarnished by absorbing oxygen. It decomposes glass at a red heat.

(628) COMPOUNDS OF BARIUM WITH OXYGEN.—Barium forms two oxides, a protoxide, baryta,  $BaO$ , and a dioxide,  $BaO_2$ ; the first is the only one which forms salts.

*Baryta*, or *Baric oxide* ( $BaO = 153.0$ ); *Sp. Gr.* 5.456.—Anhydrous baryta may be obtained by exposing baric nitrate to a red heat in a capacious porcelain crucible; the salt decrepitates, melts, and then boils up and gives off a large quantity of oxygen mixed with nitrogen, leaving the baryta as a grey porous mass, which absorbs moisture and carbonic acid if exposed to the air. If mixed with one-eighth of its weight of water it slakes, forming a hydrate, with extrication of great heat. Baryta may be fused before the oxyhydrogen blowpipe.

Baric sulphide may be employed for procuring pure *baric hydrate* (*hydrate of baryta*) by boiling its solution with cupric oxide: baric hyposulphite and cupreous sulphide, both of which are insoluble, are produced, and baric hydrate is dissolved;  $6BaS + 6H_2O + 8CuO = 5(BaH_2O_2) + BaS_2H_2O_4 + 4Cu_2S$ : the hot liquid is filtered, and crystals of the hydrate ( $BaH_2O_2, 8H_2O$ ; *Sp. Gr.* 1.656) are deposited as the solution cools. Crystals of baric hydrate may also be obtained by adding to a boiling solution of caustic soda, of sp. gr. 1.12, an equivalent quantity of baric nitrate in small quantities at a time. The hot solution is

filtered into a vessel covered from the air, and the hydrate is deposited as the liquid cools. The crystals are soluble in 3 times their weight of boiling water, and in 20 of cold water; the liquid has a strongly alkaline reaction. When exposed to the air, both the crystals and the solution absorb carbonic acid; by heat,  $8\text{H}_2\text{O}$  are expelled from the crystals, and a monohydrate is left,  $\text{BaH}_2\text{O}_2$ , of sp. gr. 4.495; it fuses at a heat above redness, and retains its water at all temperatures. Baric hydrate is sparingly soluble in alcohol.

*Baric dioxide, or Peroxide of barium* ( $\text{BaO}_2 = 169$ ) is formed by passing oxygen over anhydrous baryta at a low red heat; or by mixing pure baryta with an equal weight of potassic chlorate and heating to low redness; in the latter case ignition commences at one point, and spreads through the mass like tinder;  $3\text{BaO} + \text{KClO}_3 = \text{KCl} + 3\text{BaO}_2$ : the potassic chloride may be dissolved out by water, and a bulky white hydrated baric peroxide ( $\text{BaO}_2 \cdot 6\text{H}_2\text{O}$ ), insoluble in water, remains. Brodie, however, finds that it is impossible to convert much more than half the baryta into peroxide by either of these methods. In order to obtain the pure peroxide, he recommends (*Phil. Trans.* 1863, 409) that the crude material be completely converted into hydrate by pulverizing finely in a mortar, and rubbing it with water. It is then to be mixed gradually with a very dilute solution of hydrochloric acid, taking care that the acid is always in excess. The solution is to be filtered, and rendered slightly alkaline by the addition of baryta water, which separates alumina and ferric oxide. The alkaline solution is to be filtered as rapidly as possible through linen filters, and an excess of baryta water added to the clear filtrate; baric dioxide is thus precipitated in brilliant plates, which are insoluble in water, and may be washed by decantation; if pressed between blotting-paper it may be rendered anhydrous by desiccation *in vacuo* over sulphuric acid. It is then quite stable, and appears as a fine white powder resembling magnesia.

By strong ignition baric dioxide again parts with its oxygen. Boussingault (*Ann. de Chimie*, III. xxxv. 5) even proposed to make use of caustic baryta as a means of preparing oxygen on a large scale by alternately passing atmospheric air over the baryta raised to a dull red heat, and then expelling the absorbed oxygen by intense ignition: the presence of a small quantity of aqueous vapour greatly assists the expulsion of the oxygen, but the process cannot be worked with facility. The anhydrous peroxide combines with water when moistened, without evolving any sensible amount of heat, and crumbles down to a white powder: it is used for procuring hydric peroxide (485). Baric peroxide becomes white hot when heated over a spirit-lamp in a rapid current of carbonic or of sulphuric anhydride; small white flames burst out from its surface, whilst baric carbonate or sulphate is formed.

(629) SULPHIDES OF BARIUM.—Of these the most important is

the *protosulphide* ( $\text{BaS} = 169$ ). The preparation of this substance from the native baric sulphate presents some interest to the chemist, for it enables him to obtain with ease the soluble salts of barium from its insoluble sulphate. In order to prepare the sulphide, either the native or the artificial sulphate is reduced to a very fine powder, and intimately mixed with an equal weight of starch or flour or with one-tenth of its weight of powdered charcoal; this is made up into a paste with oil, and introduced into a crucible lined with charcoal: the cover is luted on, and the crucible and its contents are exposed for an hour to an intense heat. By this treatment the baric sulphate is deoxidized, carbonic oxide escaping, whilst baric sulphide remains:  $\text{BaSO}_4 + 4\text{C} = \text{BaS} + 4\text{CO}$ . When the mass thus obtained is treated with successive small quantities of boiling water, the sulphide is decomposed; the first portions of the solution have a yellow colour, owing to the formation of hydrosulphate of the sulphide of barium, which absorbs oxygen and becomes partially converted into baric disulphide, whilst the latter washings contain gradually increasing quantities of baric hydrate;  $2\text{BaS} + 2\text{H}_2\text{O} = \text{BaS}_2\text{H}_2\text{S} + \text{BaH}_2\text{O}_2$  and  $2(\text{BaS}_2\text{H}_2\text{S}) + \text{O}_2 = 2\text{BaS}_3 + 2\text{H}_2\text{O}$ ; but if the mass be treated with a sufficient quantity of boiling water, it becomes entirely dissolved, and the sulphide is deposited as the solution cools in colourless transparent crystals, with  $6\text{H}_2\text{O}$ . When treated with hydrochloric or any other acid, baric sulphide is decomposed, and the corresponding barium salt is formed, whilst sulphuretted hydrogen escapes; for instance,  $\text{BaS} + 2\text{HCl} = \text{BaCl}_2 + \text{H}_2\text{S}$ .

(630) **BARIC CHLORIDE**, or *Chloride of barium* ( $\text{BaCl}_2, 2\text{H}_2\text{O} = 208 + 36$ ); *Sp. Gr., cryst.* 2.664; *Anhydr.* 3.750; *Comp. in 100 parts*, Ba, 65.86; Cl, 34.14.—This salt is obtained by dissolving the baric sulphide or carbonate in hydrochloric acid. On the large scale it may be procured by fusing together 1 part of crude calcic chloride (the residue of the preparation of ammoniacal sesquicarbonate) with 2 parts of powdered native baric sulphate; baric chloride and calcic sulphate are formed; the chloride is washed out rapidly with hot water, and purified by crystallization. Baric chloride crystallizes in flat four-sided tables, containing  $2\text{H}_2\text{O}$ , which may be expelled by heat: water dissolves nearly half its weight at  $59^\circ$  ( $15^\circ \text{C.}$ ), and three-fourths at  $212^\circ$  ( $100^\circ \text{C.}$ ): the presence of hydrochloric or of nitric acid greatly diminishes its solubility. A solution of this salt is the usual test for ascertaining the presence of a sulphate in solutions, which it indicates by the formation of a white precipitate insoluble in nitric acid. If anhydrous baryta be introduced into a jar of hydro-

chloric acid gas it becomes incandescent, baric chloride is formed, and water becomes condensed on the sides of the vessel.

(631) **BARIC SILICOFLUORIDE** ( $\text{BaF}_2, \text{SiF}_4 = 279$ ) is procured by adding silicofluoric acid to a solution of a baric salt; it is quickly deposited in microscopic crystals, which are insoluble in an excess of the acid. The salt is anhydrous. It is decomposed by ignition, which converts it into baric fluoride. Strontic silicofluoride is soluble, and hence silicofluoric acid may be employed to distinguish salts of barium from those of strontium.

(632) **BARIC SULPHATE, OR SULPHATE OF BARIUM** ( $\text{BaSO}_4 = 233$ ); *Sp. Gr.* 4.59; *Comp. in 100 parts*,  $\text{BaO}$ , 65.66;  $\text{SO}_3$ , 34.34.—This is the principal native mineral of baryta. It occurs in the mountain limestone in large veins, and is found accompanying the ores of lead and other metals. It is met with both massive, and crystallized in modifications of the right rhombic prism. The name 'baryta' is derived from  $\beta\alpha\rho\upsilon\varsigma$ , heavy, in allusion to the high specific gravity of this compound, which is about 4.6. It is insoluble in water, and in all the acids except boiling concentrated sulphuric acid: as the solution in this acid cools, crystals of the sulphate are deposited. De Senarmont found that when the recently precipitated sulphate is heated to  $482^\circ$  ( $250^\circ \text{C.}$ ), for 60 hours in a sealed tube, with diluted hydrochloric acid, or with a solution of hydrosodic carbonate (bicarbonate), microscopic crystals of the same form as those of the native baric sulphate are deposited upon the sides of the tube. I have observed the formation of similar crystals when a very dilute solution of baric chloride (1 part in 10,000) is mixed with a small proportion of sulphuric acid at ordinary temperatures. At a bright red heat the sulphate fuses into a white enamel: and by boiling the powdered baric sulphate with either potassic or sodic carbonate, or, more rapidly by fusing it with either of these salts, the artificial sulphate is partially converted into the carbonate. It may be easily formed by precipitating a solution of any barium salt with any soluble sulphate, when it falls as a heavy white powder. If nitric acid or any nitrate be present in the solution, the precipitate carries down with it a portion of the nitrate, and this can only be removed by long washing with boiling water. Baric sulphate is used as a *permanent white* by artists in water colours. It is also employed for adulterating white lead; when ground with oil, however, it becomes partially transparent, and impairs the opacity of the lead pigment.

(633) **BARIC NITRATE, OR Nitrate of barium** ( $\text{Ba}_2\text{NO}_3 = 261$ ); *Sp. Gr.* 3.284; *Comp. in 100 parts*,  $\text{BaO}$ , 58.62;  $\text{N}_2\text{O}_5$ , 41.38) crystallizes in anhydrous octohedra, when a solution of the baric carbonate in nitric acid is evaporated. It is insoluble in alcohol,

and requires eight or ten times its weight of cold water, and 3 of boiling water, for solution. Nitric acid precipitates it in crystals from its solution, unless very dilute: when heated, it first decrepitates strongly, and afterwards fuses; on ignition, the whole of the acid is expelled, with an appearance of ebullition owing to the escape of oxygen and nitrogen, whilst pure baryta remains.

(634) **BARIC CARBONATE**, or *Carbonate of barium* ( $\text{BaCO}_3 \equiv 197$ ); *Sp. Gr.* 4.3; *Comp. in 100 parts*, BaO, 77.69;  $\text{CO}_2$ , 22.31.—This compound forms the mineral called *witherite*: it occurs, both massive and crystallized, usually in six-sided prisms terminated by six-sided pyramids. It is abundant in the lead-veins in the north of England, and is also found in Styria and in Siberia. It is easily prepared artificially by precipitating a barium salt by the carbonate of one of the alkali-metals; it then forms a white powder, which is very sparingly soluble in pure water, and is insoluble in water charged with saline matter: an aqueous solution of carbonic acid dissolves it rather freely. If suspended in a solution of potassic or sodic sulphate, in the cold, and frequently agitated, freshly precipitated baric carbonate is converted into sulphate; but if baric sulphate be boiled with a carbonate of one of the alkali-metals, carbonate of barium and sulphate of the alkali-metal are produced. Ignition of the carbonate does not expel the carbonic acid, but if it be mixed with charcoal and intensely ignited, it is partially decomposed; pure baryta is obtained, and may be dissolved out with water. If mixed with an equal weight of calcic carbonate, baric carbonate is decomposed without much difficulty when ignited in a current of steam, a mixture of baric and calcic hydrates being formed; baric hydrate may be dissolved out of the mixture by water.

Baric carbonate is now manufactured to some extent as a substitute for a portion of the alkali and oxide of lead in the making of plate and flint glass: the baric silicate which is formed fuses and becomes incorporated with the other silicates. The carbonate is prepared for this purpose from the sulphate, which is reduced to the form of sulphide by ignition with carbonaceous matter: the sulphide is then dissolved in water, and decomposed by a current of carbonic acid, which precipitates the baric carbonate as a fine white powder.

(635) **CHARACTERS OF THE SALTS OF BARIUM.**—The barium salts with colourless acids are colourless. The carbonate and all the soluble salts act as powerful poisons, and have an acrid, disagreeable taste. The best antidote when they have been taken internally is sodic or magnesian sulphate.



Barium salts when in solution are easily recognized by giving with *sulphuric acid* a white precipitate of baric sulphate, which is insoluble in the acids. Barium is, for the purposes of analysis, usually estimated in the form of sulphate; 100 parts correspond to 65.66 of BaO and 34.34 of SO<sub>3</sub>. The presence of citrate either of sodium or ammonium prevents the precipitation of baric sulphate in neutral and alkaline solutions; but these salts do not redissolve the baric sulphate after it has once been deposited. On acidulating with hydrochloric acid the solution containing the citrates, baric sulphate is precipitated in the usual manner (Spiller).

With *potassic* or *sodic carbonate* a white precipitate of baric carbonate is produced in solutions which contain barium. *Ammonic hydrosulphide* gives no precipitate in such solutions. *Hydrodisodic phosphate* gives a white precipitate which is soluble in diluted nitric or hydrochloric acid. Soluble barium salts, when mingled with alcohol, tinge its flame of a yellowish-green colour. In the spectroscope the spectrum of the barium salts is distinguished by a remarkable series of bright bands in the green, with fainter bands in the red. (Part I., fig. 83, *Ba*, page 180). Barium salts are distinguished from those of strontium by forming an insoluble baric silicofluoride when mixed with *silicofluoric acid*; and by yielding no immediate precipitate with *oxalic acid*, but the mixture on standing deposits tufts of acicular crystals of acid oxalate of barium. A solution of *sodic hyposulphite* occasions a crystalline precipitate of the sparingly soluble baric hyposulphite.

## § II. STRONTIUM: (Sr' = 87.5). *Sp. Gr.* 2.54

(636) STRONTIUM is an element much less abundantly diffused than barium, which it closely resembles in properties. It is found both as carbonate and as sulphate, and is procured in the metallic state in the same way as barium, to which it bears a relation similar to that existing between potassium and sodium. Strontium is a malleable metal of a pale yellow colour. When heated in the air, it burns with a crimson flame, emitting sparks. Water is decomposed by it with evolution of hydrogen: diluted nitric acid dissolves it, but the concentrated acid is almost without action even when boiled upon it.

(637) STRONTIA (SrO = 103.5; *Sp. Gr.* 4.61) may be obtained from its nitrate by ignition. When mixed with water it makes, and forms a crystalline hydrate (SrH<sub>2</sub>O<sub>4</sub>.8H<sub>2</sub>O; *sp. gr.* 1.396): these crystals require 50 times their weight of cold and 24 of boiling water for solution; 8H<sub>2</sub>O are easily expelled by heat, the remaining atom requiring a much higher temperature for its expul-

gion; at a red heat the latter hydrate fuses, furnishing a mass of sp. gr. 3·625: both the hydrate and its solution absorb carbonic acid rapidly from the air. No peroxide of strontium can be formed.

(638) STRONTIC CHLORIDE, or *Chloride of strontium* ( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O} = 108\cdot5 + 198$ ; *Sp. Gr. anhydrous*, 2·96, *cryst.* 1·603) crystallizes in slightly deliquescent needles, which require less than their weight of cold water for solution; alcohol dissolves it, and the solution burns with a crimson flame. Strontic chloride is rendered anhydrous by a moderate heat; if heated strongly it fuses.

*Strontic silicofluoride* ( $\text{SrF}_2 \cdot \text{SiF}_4 = 229\cdot5$ ) is prepared by adding hydrofluosilicic acid to a salt of strontium: it is tolerably soluble in water, thus furnishing a character which distinguishes the compounds of strontium from those of barium.

(639) STRONTIC SULPHATE, or *Sulphate of strontium* ( $\text{SrSO}_4 = 183\cdot5$ ; *Sp. Gr.* 3·9); *Comp. in 100 parts*,  $\text{SrO}$ , 56·52;  $\text{SO}_3$ , 43·48.—This substance is found crystallized in rhombic prisms isomorphous with those of baric sulphate; it is, however, easily distinguished from it by its lower density. Many specimens of this mineral have a delicate blue tint, whence it derives its mineralogical name of *celestine*: it often contains crystals of native sulphur. Strontic sulphate is very sparingly soluble in water, but is taken up by boiling sulphuric acid, and is soluble to some extent in a solution of sodic chloride. It may be formed by mixing a solution of any sulphate with a solution of a strontium salt.

(640) STRONTIC NITRATE, or *Nitrate of strontium* ( $\text{Sr}_2\text{NO}_3 = 211\cdot5$ ; *Sp. Gr. anhydr.* 2·857, *cryst.* 2·113) crystallizes from hot concentrated solutions in anhydrous octohedra, which are soluble in 5 parts of cold water and half their weight of boiling water; by crystallizing it at a low temperature it may be obtained in efflorescent crystals with  $5\text{H}_2\text{O}$ . If strongly heated, it decrepitates, and then is decomposed with loss of oxygen and nitrogen, leaving pure strontia. It is used by the makers of fireworks to give a splendid crimson colour to their flames, and is prepared for them by reducing the native sulphate to sulphide by heating it with charcoal, dissolving the sulphide in water, and decomposing it with diluted nitric acid. It crystallizes best from an acid solution. A mixture of 40 parts of strontic nitrate with from 5 to 10 of potassic chlorate, 13 of sulphur, and 4 of antimonious sulphide, deflagrates with a magnificent red colour; the mixture is dangerous both to prepare and to preserve, having more than once been the occasion of frightful accidents to the manufacturers, from its becoming ignited spontaneously. Strontic nitrate is insoluble in alcohol.

(641) STRONTIC CARBONATE ( $\text{SrCO}_3 = 147\cdot5$ ); *Sp. Gr.* 3·65; *Comp. in 100 parts*,  $\text{SrO}$ , 70·2;  $\text{CO}_2$ , 29·8.—This compound

forms the *strontianite* of mineralogists; it occurs both massive and crystallized, near Strontian in Argyleshire, and hence the name 'strontia' given to the earth which it contains. Mere ignition is insufficient to decompose this salt. It is scarcely soluble in water, but is dissolved by a solution of carbonic acid. The process of preparing it consists in precipitating a strontium salt by the carbonate of one of the alkali-metals.

(642) **CHARACTERS OF THE STRONTIUM SALTS.**—The strontium salts with colourless acids are all colourless: they have a bitter acrid taste, but are not poisonous. They are distinguished *before the blowpipe* by the red colour which they communicate to the flame. By the spectroscope they are seen to furnish several bright bands in the red and orange part of the spectrum, and a brilliant band in the blue. (Fig. 83, *Sr*, Part I. p. 180.) The flame of strontium to the unaided eye seems to have the same colour as that of lithium, but the spectra of the two cannot be confounded. Reagents produce upon strontium salts the same effects as upon salts of barium, excepting that neither *silicofluoric acid* nor *sodic hyposulphite* yields any precipitate in the solutions of strontium salts. *Oxalic acid* gives an immediate turbidity in them. The compounds of strontium are distinguished from those of calcium by the gradual formation of a white precipitate on agitation after the addition of a solution of *calcic sulphate*. Strontic sulphate is used for determining the amount of strontia in analysis; 100 parts of it correspond to 56.52 of strontia.

### § III. CALCIUM: ( $\text{Ca}''=40$ .) *Sp. Gr.* 1.578.

(643) **CALCIUM** forms one of the most abundant and important constituents of the crust of the globe. It derives its name from *calx*, lime, of which earth it is the metallic basis. Calcium occurs in nature in combination with fluorine, forming the different varieties of fluor-spar; it is still more abundant in the various forms of calcic carbonate; and it is also met with in large quantities as gypsum, which is a hydrated calcic sulphate.

Calcium was obtained by Matthiessen (*Q. J. Chem. Soc.* viii. 27) by the electrolytic decomposition of a mixture consisting of 2 equivalents of calcic chloride and 1 equivalent of strontic chloride. The mass may be fused in a Hessian crucible, in the centre of which is placed a porous tube filled with the same mixture, and into this an iron wire passed through the stem of a tobacco-pipe is inserted. This wire is connected with the platinode of the battery, the zincode of which consists of a plate of sheet-iron bent into a cylindrical form, and immersed in the melted mass exterior to the porous tube: the calcium is reduced, and preserved from oxidation by so regulating the heat that a film of solidified salt

shall form upon the surface of the mixture in the porous cell. Lies Bodart obtains it still more easily by fusing calcic iodide with an equivalent quantity of sodium.

Calcium is a light, yellowish metal, of the colour of gold largely alloyed with silver: in hardness it is intermediate between lead and gold; it is very malleable, and can readily be hammered into leaves thinner than writing paper. It melts at a red heat. At ordinary temperatures it tarnishes within a day or two, even in dry air, and in the presence of moisture it is slowly oxidized. When heated to redness on platinum foil, it burns with a brilliant scintillating white light. It readily amalgamates with mercury: when heated in chlorine, or in the vapour of bromine, iodine, or sulphur, combustion occurs, accompanied by an extremely vivid light. Water is rapidly decomposed by calcium, calcic hydrate being formed and hydrogen evolved. Concentrated nitric acid does not attack the metal until heated to the boiling-point, though the diluted acid dissolves it rapidly. Matthiessen found that calcic chloride is not decomposed by heating it with potassium or sodium; and he concludes that the properties formerly assigned to calcium were really due to a mixture of potassium with aluminum and silicon.

(644) LIME; *Calcic oxide* ( $\text{CaO} = 56$ ); *Sp. Gr.* 3.18; *Comp. in 100 parts*, Ca, 71.43; O, 28.57.—Calcium forms only one oxide—viz., lime, which has been known from time immemorial. It is obtained in a state of purity by heating pure calcic carbonate (654) to full redness; this carbonate occurs very nearly pure either in black or in Carrara marble, which if burnt for an hour or two in an open fire—or better still, in a crucible with a hole at the bottom—yields lime very nearly free from foreign matters. For commercial purposes, common limestone, which is an impure calcic carbonate, is burned in a kiln, the cavity of which is usually egg-shaped. Over the fire-grate an arch is formed with lumps of limestone, and the kiln is filled up with smaller fragments, the fire is then kindled below, and kept up continuously for three days and nights; the kiln is then allowed to cool, the lime is removed, and a fresh charge introduced. A better method is that known as the continuous process. The kiln in this case is in the form of an inverted truncated cone: it is charged with alternate layers of coal and limestone, and the fire is kindled. The lime, as it is burned, gradually sinks down, and is removed by openings at the base of the furnace, and a fresh supply of coal and limestone is supplied at the top of the kiln. The limestone should not be too dry; that which has been quarried recently answers best. In damp weather, too, the operation succeeds better than in a dry state of the atmosphere; indeed, the process is facilitated by injecting steam into the kiln, although in practice the advantage which is gained does not compensate for the increased expense and trouble. In the presence of aqueous vapour an interchange between the steam and the carbonic anhydride of the limestone appears to be effected, and calcic hydrate is

formed; but the hydrate which is produced is quickly destroyed again.

Pure lime, or *quicklime*, is a white caustic powder which may be heated without fusing even in the oxyhydrogen flame; and emits an intense white light when thus ignited, as is seen in its application to the Drummond light. The extreme infusibility of lime has led Deville to employ it as a material for lining crucibles which are to be exposed to very intense heat.

*Calcic hydrate, Hydrate of lime, or Slaked lime* ( $\text{CaH}_2\text{O}_2=74$ ); *Sp. Gr.* 2.078; *Comp. in 100 parts*,  $\text{CaO}$ , 75.68;  $\text{H}_2\text{O}$ , 24.32.—When water is poured upon lime, the earth swells up and enters into combination with the water; if the proportion of water be not too great, a light dry powder is formed, attended with a powerful extrication of heat: so great is the heat thus developed that fires have several times been traced to this source. The hydrate which is formed is a definite compound of 1 atom of water with 1 of lime. Lime, when exposed to the air, slowly attracts both water and carbonic anhydride; as a result of this action it falls to powder, and becomes what is termed *air slaked*; in this case a compound is gradually formed, which is by some chemists regarded as a combination of an atom of calcic carbonate with one of hydrate ( $\text{CaO}, \text{CO}_2, \text{CaO}, \text{H}_2\text{O}$ ).

Lime is soluble in about 700 parts of cold water; this solution is known as lime-water; the earth, however, is less soluble in hot than in cold water, so that if lime-water saturated in the cold be raised to the boiling-point, half the lime is deposited. Lime is much more soluble in syrup than it is in water; the solution in this case also becomes turbid when heated, but clears again as it cools. Lime-water is much employed as a test for the presence of carbonic acid, which instantly renders it turbid: it has a distinctly alkaline reaction, and an acrid taste: by evaporating it *in vacuo*, Gay-Lussac obtained from it calcic protohydrate crystallized in hexahedral plates. Calcic hydrate is decomposed by a red heat, and pure lime remains.

*Milk of lime* is merely hydrated lime diffused through water: in slaking lime for its preparation, and, indeed, generally where small quantities of the hydrate are required in a fine state of subdivision, it is best to use boiling water in quantity nearly equal to twice the weight of the lime; the powder may afterwards be readily diffused through cold water.

(645) *Mortars and Cements*.—The great consumption of lime in the arts is for the purpose of making mortars and cements. Pure lime, when made into a paste with water, forms a somewhat

plastic mass, which sets into a solid as it dries, but it gradually cracks and falls to pieces. It does not possess sufficient cohesion to be used alone as a mortar; to remedy this defect and to prevent the shrinkage of the mass, the addition of sand is found to be necessary. Ordinary mortar is prepared by mixing 1 part of lime into a thin paste with water, and adding 3 or 4 parts of sharp sand, of tolerable fineness: the materials are then thoroughly incorporated, and passed through a sieve to separate lumps of imperfectly burned lime: a suitable quantity of water is afterwards worked into it, and it is then applied in a thin layer to the surfaces of the stones and bricks which are to be united. The bricks or stones are moistened with water before applying the mortar, in order that they may not absorb the water from the mortar too rapidly. The completeness of the subsequent hardening of the mortar depends mainly upon the thorough intermixture of the lime and sand.

The theory of the hardening of mortar is obscure. The mortar gradually becomes dry upon its surface, and at the same time it absorbs carbonic anhydride from the air; but this change is rarely complete, for the central portions, after a lapse of many ages, are still found to contain free lime in abundance: mortar taken by Dr. Malcolmson from the Great Pyramid, was still found to contain a large proportion of lime as hydrate. A gradual combination also takes place between the lime and the silica of the sand: each grain of sand thus becomes superficially converted into a hydrated calcic silicate, forming a compound which by degrees acquires considerable hardness, and contributes greatly to the solidification of the mortar. All old mortar, when treated with an acid, yields a small proportion of gelatinous silica. A mixture of calcic carbonate with the lime appears to set harder than pure lime only; so that for many purposes lime which has been slaked by exposure to the air, and contains a considerable proportion of carbonate, is preferred to that slaked rapidly by water.

Limestones vary greatly in composition; being rocks of sedimentary origin, they are not pure chemical compounds, but consist of a mixture of various bodies, in which calcic carbonate is the prevailing ingredient. The different varieties of limestone are distinguished according to the nature of the most important of these admixtures: a limestone, for example, is described as magnesian, argillaceous, ferruginous, sandy, or bituminous, according as it is characterized by the presence of magnesian carbonate, clay, ferric oxide, sand, or bituminous matter. These different limestones, when burned, yield lime of very different qualities, which

are particularly manifested by the action of water upon the lime produced. The purer the lime, the more quickly does it combine with water when mixed with it. Such pure limes are technically termed *rich* or *fat* limes; when the amount of impurities present does not exceed 10 per cent. they slake rapidly, during which operation they swell up and greatly increase in bulk; they become extremely hot, and yield a soft, fine, dense paste; while those which contain much magnesia, silica, or alumina, slake slowly, emit but little heat, and are technically termed *poor*.

In slaking for mortar, a fine smooth paste is required: in order to secure this condition, the slaking should be effected quickly, with about 3 parts of water to 1 part of lime; the mass, if composed of a fat lime, then swells to between three and four times its former bulk: if too little water be used, a crystalline granular hydrate is formed.

The temperature required for burning lime varies with the composition of the limestone. When a siliceous limestone is burnt, the silica combines with the lime if the temperature be too high and be too suddenly raised, and a coating of silicate forms on the surface of the mass, which becomes partially vitrified. Such lime slakes very imperfectly, and is said to be *dead burnt*. If ordinary quicklime be mixed with a small quantity of calcic sulphate, or if it be re-burnt at a dull red heat in an atmosphere containing a small proportion of sulphurous anhydride, it acquires the property of setting slowly like stucco when mixed with cold water, but if boiling water be used it slakes like common lime. Lime so prepared is known as *Scott's cement*.

(646) *Hydraulic Mortars*.—Ordinary mortar, when placed in water, becomes gradually softened and disintegrated, whilst the lime is dissolved away. It cannot therefore be used for sub-aqueous constructions. Some poor limes, however, which contain from 15 to 35 per cent. of finely divided silica or clay, form what are termed *hydraulic limes*: when mixed with a due proportion of sand (from 1.5 to 1.8 times their weight) they furnish a mortar which possesses the valuable property of hardening under water. These limes may be artificially imitated by mixing with the lime a due proportion of clay not too strongly burnt. At Puzzuoli, near Naples, a porous volcanic material, which has received the name of *puzzuolana*, is found. This substance, when powdered and mixed with ordinary lime, confers upon it the property of yielding an excellent hydraulic mortar, which was employed by the Romans in many of their buildings, in which it is still in perfect preservation, having resisted the ravages of time more perfectly than the bricks which it was used to cement. It is found that a *puzzuolana* which is easily attacked by sulphuric acid is more effective than one which resists the action of the acid. The comparative value of a *puzzuolana* may also be roughly

and rapidly estimated by taking a given measure of lime-water, and agitating it with successive small quantities of finely powdered puzzuolana until the alkaline reaction disappears; the puzzuolana combines with the lime and abstracts it from the water. The smaller the quantity of the powder required, the more active are its hydraulic powers. Puzzuolana consists chiefly of silicates of aluminum, calcium, and sodium.

Many other substances, when added to lime, confer upon it hydraulic properties to a greater or less extent. Gelatinous silica shows this power slightly, and a mixture of hydrated silica with freshly precipitated alumina or magnesia shows it in a remarkable degree. Sand, ferric oxide, and black oxide of manganese, are destitute of this property. From a knowledge of these facts it is easy to convert ordinary lime into one possessed of hydraulic properties. Clay is an aluminic silicate; when it is heated with lime, decomposition occurs, the alumina is set free, and calcic silicate is formed. The materials are in this way reduced to a condition suitable for use, without the addition of sand, as a hydraulic cement; but great care is required in regulating the temperature. If it be allowed to rise too high, partial vitrification occurs, which impairs the tendency of the cement to combine with water; while, on the other hand, if the heat be insufficient, the alumina is not liberated from its combination with the silica. The immediate cause of the solidification of these hydraulic limes appears, according to the experiments of Fremy and others, to be the formation of a hydrated compound of lime with the alumina, which is very hard, and insoluble in water.

Hydraulic limes do not slake with any considerable emission of heat when moistened; they absorb the water without increasing much in bulk, and form a paste of small plasticity. In order that a hydraulic mortar may harden properly, it must not be submerged till it begins to set; it should then be kept moist until it is quite hard, otherwise it will always remain porous.

The manufacture of artificial hydraulic cement was first established upon sound principles by Vicat. He proceeds thus in its preparation:—Four parts of chalk are ground and levigated in water with 1 part of clay, so as to obtain a very intimate mixture of the materials, which are allowed to subside, moulded into blocks, dried, and calcined at a carefully regulated temperature. *Portland cement* is a hydraulic cement similar to the above. It is made from clay obtained in the valley of the Medway, and from chalk found in the same neighbourhood: it derives its name from the circumstance that in colour, when dry, it resembles Portland stone. It is prepared by thoroughly grinding the clay and chalk with water, allowing them to subside, then drying and burning the mixture until it undergoes slight vitrification; the mass is again ground, and when mixed with a proper proportion of water, it forms a cement which possesses great



hardness and tenacity; it expands as it solidifies. If in preparing this cement the lime be first burned and then mixed with clay and reburned, it does not require more than a full red heat to produce a good cement.

The rapidity with which these different kinds of hydraulic limes set, varies considerably with their composition. If the clay do not exceed 10 or 12 per cent. of the weight of the original limestone, the mortar requires several weeks to harden. If the clay amount to from 15 to 25 per cent., it sets in two or three days, and if from 25 to 35 per cent. of clay be present, the solidification occurs in a few hours. The substance to which the term *Roman cement* is now applied is a lime of this latter description. Roman cement is extensively prepared from nodules of septaria which occur in the valley of the Thames. It sets in a few hours after the mixture with water has been effected, and it soon rivals stone in hardness. According to Meyer, the composition of the nodules employed in the preparation of the cement is the following:—

Matter soluble in acid 76.0	{ Calcic carbonate ...	66.99
	{ Magnesian carbonate ...	1.67
	{ Ferrous carbonate ...	6.95
	{ Alumina ...	0.39
Insoluble in acid (clay) 23.305	{ Silica ...	16.89
	{ Alumina ...	4.32
	{ Ferric oxide ...	1.72
	{ Lime ...	0.005
	{ Magnesia ...	0.37

The cement obtained from the neighbourhood of Boulogne is almost identical in composition with the foregoing; and similar materials have been obtained in other countries, particularly in the beds of the Jurassic formation.

*Concrete* is a mixture of hydraulic mortar with small pebbles coarsely broken.

(647) *Other Uses of Lime*.—Lime is also largely employed as a manure, and it is particularly valuable upon very rich vegetable soils, such as those formed over peat bogs: its effects in these cases are partially due to the decomposition of the organic matter, which it renders soluble and capable of assimilation, while the lime itself is converted into carbonate. It has been found that limestone containing much magnesian carbonate yields a lime unsuited to agricultural purposes; this has been attributed to the fact that magnesia absorbs carbonic acid much more slowly than lime, and remains caustic for a longer period, in which state it appears to be injurious to the tender shoots of young plants.

The strong attraction existing between lime and carbonic acid renders it a valuable material for separating this acid from the

potassic and sodic carbonates, when these alkalies are required in a caustic form. The attraction of lime for water furnishes a means of removing this liquid from many substances which retain it with considerable force, such as alcohol; the finely powdered lime is mixed with the alcohol, and the mixture after being allowed to stand for a few days, with occasional agitation, is subjected to distillation: anhydrous alcohol passes over, leaving the water combined with the lime. Slaked lime is employed as a direct chemical agent in the purification of coal-gas, and as a means of loosening the epidermis, and facilitating the removal of the hair from hides, as a preliminary to the process of tanning.

Hydric peroxide forms an insoluble compound with lime, which is precipitated in crystalline scales when the peroxide is poured into lime-water: it is very unstable, and undergoes spontaneous decomposition at the temperature of the air. This substance has been described as *binoxide of calcium*.

(648) **SULPHIDES OF CALCIUM.**—Calcium forms several compounds with sulphur, some of which are soluble.

*Calcic protosulphide* ( $\text{CaS}=72$ ) is procured by decomposing a mixture of calcic sulphate and charcoal by heat as directed for preparing baric sulphide. It is insoluble in cold water, but when treated with boiling water in small proportion is converted into calcic hydrate, and a soluble calcic disulphide. Calcic protosulphide is phosphorescent when newly prepared. This property was first observed by Canton, in an impure calcic sulphide, which he obtained by calcining oyster-shells in an open fire for half an hour, then selecting the whitest and largest portions, and packing them with one-third of their weight of flowers of sulphur in a crucible with a luted cover; this was heated strongly for an hour: when cold, the crucible was broken, and the whitest pieces were placed in well-closed bottles.

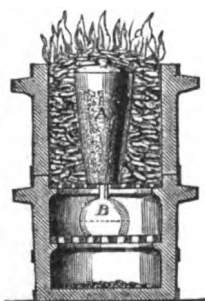
Calcic sulphide forms one of the principal constituents in the soda waste of the alkali maker. When exposed to the air in a moist state it absorbs oxygen and furnishes calcic hyposulphite in large quantity:  $2\text{CaS} + 2\text{H}_2\text{O} + 2\text{O}_2 = \text{CaO}, \text{H}_2\text{O} + \text{CaS}_2\text{H}_3\text{O}_4$ .

By boiling slaked lime with excess of sulphur, *calcic pentasulphide* is obtained, and calcic hyposulphite is formed at the same time:  $3\text{CaO} + 6\text{S}_8 + \text{H}_2\text{O} = 2\text{CaS}_5 + \text{CaS}_2\text{H}_3\text{O}_4$ .

(649) **CALCIC PHOSPHIDE** ( $\text{CaP}=71$ ).—This compound presents some interest, from its affording the most convenient source of some of the phosphides of hydrogen (455). It is prepared by distilling phosphorus over lime heated to low redness: a mixture of calcic phosphide and pyrophosphate is the result,  $7\text{P} + 7\text{CaO} = \text{Ca}_3\text{P}_2\text{O}_7 + 5\text{CaP}$  (P. Thénard). The most convenient method of

conducting the operation is shown in fig. 348. In the lower part of a narrow deep crucible, A, a hole is drilled for the reception of the neck of a flask, B, which

FIG. 348.



is luted into the aperture; a quantity of dry phosphorus is placed in the flask, and the crucible is filled with quicklime, broken into fragments of about the size of a hazelnut; a lid is then luted upon the top of the crucible. Time having been given for the luting to become dry, the upper part of the crucible is raised to a red heat as quickly as possible, by surrounding it with ignited charcoal, the lower part of the furnace having been filled with cold charcoal, to prevent the heat from reaching the phosphorus too rapidly; the phosphorus becomes gradually volatilized as the heat reaches it. If the heat be too high, the phosphorus distils over without combining with the calcium.

Calcic phosphide when procured in this manner forms an anhydrous mass of a dull red colour, hard enough to strike fire with steel: it experiences no change in dry air or in oxygen at the ordinary temperature. At a high temperature it becomes partially decomposed by oxygen, chlorine, or hydrochloric acid; in a moist atmosphere it slakes, emits phosphuretted hydrogen, and crumbles to a brown powder. This powder, when thrown into water, or heated to  $212^{\circ}$  ( $100^{\circ}$  C.), evolves phosphuretted hydrogen, which is not self-lighting, and is mixed with free hydrogen.

Calcic phosphide, in its unslaked form, is decomposed when thrown into water; phosphuretted hydrogen gas is evolved, and takes fire with the phenomenon already described (454): diluted acids produce its decomposition still more rapidly.

(649a) *Calcic Disilicide*, or *Silicide of calcium* ( $\text{Si}_2\text{Ca}$ ). — Wöhler (*Liebig's Annal.* cxvii. 257), in order to prepare this singular compound, directs 20 grammes of graphitoid-silicon to be finely powdered and intimately mixed with 200 grms. of calcic chloride in a hot mortar, and to be rapidly shaken up in a wide-mouthed bottle with 23 grms. of sodium cut into small pieces: meantime a Hessian crucible is to be brought to a full red heat in a good wind-furnace; a little fused common salt is to be thrown into the crucible, and upon this a mass of sodium of 23 grms.; then the mixture of silicon and sodium and calcic chloride, and the whole is covered with a layer of pulverized fused sodic chloride: after this the cover is put on; the fire is then gradually raised, and maintained for half an hour at a temperature sufficient to melt cast iron. On breaking the crucible after it has cooled, the calcic disilicide ought to be found in the form of a well-fused button, which must be preserved in well-closed vessels.

Calcic disilicide has a leaden-grey metallic lustre and a scaly crystalline structure, with an indistinct indication of hexagonal plates. When exposed to the air it crumbles down slowly into a mass of graphite-like plates. If thrown into water a similar change occurs, attended with a very gradual but prolonged disengagement of hydrogen. This disintegration is due to the hydration and oxidation of part of the calcium and silicon, the new products remaining mixed with some unaltered silicide. Fuming nitric acid does not attack the calcic disilicide. Hydrochloric acid, as well as dilute sulphuric and acetic acids, converts it into the yellow substance already described (471), whilst hydrogen escapes.

Calcic disilicide has, in the hands of Wöhler, proved a source from which he has been enabled to procure various compounds of silicon, hydrogen, and oxygen, presenting some analogy with the compounds of carbon with the same elements, and will probably give rise to further researches of importance.

(650) *CALCIC CHLORIDE*, or *Chloride of calcium*, ( $\text{CaCl}_2$ ),

$6\text{H}_2\text{O} = 111 + 108$ ; *Sp. Gr. fused*, 2.485, *cryst.* 1.680; *Comp. in 100 parts*, Ca, 36.03; Cl, 63.97.—This salt is obtained as a secondary product in the manufacture of carbonate from chloride of ammonium, but it may be prepared by dissolving chalk in hydrochloric acid, evaporating to dryness, and fusing the residue at a red heat. Under these circumstances, a small portion of the chlorine is displaced by the oxygen of the air, so that the mass has an alkaline reaction, owing to the presence of lime. By evaporation of its solution the chloride may be obtained in striated prismatic six-sided crystals with  $6\text{H}_2\text{O}$ , which fuse at  $84^{\circ}.2$  ( $29^{\circ}\text{C.}$ ). In this form it produces great depression of temperature when dissolved in water, and if mixed with snow it furnishes a powerful freezing mixture. If the hydrated salt be exposed to a prolonged heat of  $302^{\circ}$  ( $150^{\circ}\text{C.}$ ) it forms a porous mass which still retains  $2\text{H}_2\text{O}$ ; in this state it is well adapted for the desiccation of gases. Calcic chloride is extremely deliquescent; a saturated solution of the salts boils at  $355^{\circ}$  ( $179^{\circ}.5\text{C.}$ ), and is sometimes employed where a steady temperature, not exceeding this point, is required. It is soluble in alcohol, and may be obtained from its alcoholic solution crystallized in rectangular plates ( $\text{CaCl}_2, 4\text{C}_2\text{H}_6\text{O}$ ) containing 4 atoms of alcohol. Calcic chloride absorbs ammonia rapidly, and forms a compound with 8 atoms of the gas. A solution of the chloride, if boiled with quicklime and filtered while hot, deposits long, flat, thin crystals of a hydrated oxychloride, consisting of  $(\text{CaCl}_2, 3\text{CaO}, 15\text{H}_2\text{O})$ , which is decomposed both by water and alcohol.

*Calcic iodide* ( $\text{CaI}_2$ ).—This is a soluble colourless compound, which may be obtained by dissolving chalk in hydriodic acid, and evaporating the solution rapidly to dryness in a vessel in which it is excluded from the air.

(651) **CALCIC FLUORIDE**, or *Fluoride of calcium* ( $\text{CaF}_2 = 78$ ); *Sp. Gr.* 3.14; *Comp. in 100 parts*, Ca, 51.28; F, 48.72.—This is an abundant mineral, well known as *fluor-spar*, which occurs either massive, or crystallized in forms allied to the cube. It is found accompanying the lead veins in Cumberland, Derbyshire, and Cornwall, and is met with in a variety of other localities, of various colours, most frequently blue, green, or white. Fluor-spar is the principal source from which the compounds of fluorine are obtained. Calcic fluoride, in minute quantity, is found in sea-water, and in many springs: it is a never-failing companion of calcic phosphate in the bones and teeth of animals, and indeed is always found to accompany calcic phosphate in the mineral kingdom also, in small but variable quantities. Most varieties of fluor-spar, when gently heated,

become phosphorescent, emitting a pale green or violet light ; if heated more strongly, the crystals decrepitate, and each fragment becomes enveloped for a few seconds in a beautiful halo of light. It loses this property after having been once heated ; a phosphorescent fluor, dissolved in hydrochloric acid and precipitated by ammonia, retains its power of emitting light when heated, but if it had been previously heated sufficiently to destroy the phosphorescence, this property is not restored by solution and reprecipitation.

Powdered fluor-spar absorbs sulphuric acid if mixed with it at a low temperature, and forms a transparent, viscous mass, from which fumes of hydrofluoric acid are evolved by heating it to  $104^{\circ}$  ( $40^{\circ}$  C.). Fluor-spar undergoes no change when heated with sulphuric anhydride, but with boracic anhydride it yields calcic diborate and boric trifluoride ;  $3\text{CaF}_2 + 4\text{B}_2\text{O}_3 = 3(\text{Ca}_2\text{B}_4\text{O}_{14}) + 2\text{BF}_3$ . Hydrochloric acid dissolves it in small quantity. If heated in a current of chlorine, a gas which corrodes glass is expelled. It is not known whether this is fluorine or chloride of fluorine. When fluor-spar is fused with the hydrated alkalis it undergoes no change : with the carbonates of the alkali-metals, fluoride of the alkali-metal and calcic carbonate are formed. If heated with calcic sulphate, it fuses and forms a glass which is transparent when hot, but enamel-white when cold. In proper proportions it often forms a valuable flux in smelting the ores of various metals, and hence the name *fluor* is derived, though it requires rather an elevated temperature to fuse it when heated without any admixture.

(652) CALCIC SULPHATE, OR SULPHATE OF CALCIUM ( $\text{CaSO}_4 = 136$ ) ; *Sp. Gr.* 2.95 ; *Comp. in 100 parts*,  $\text{CaO}$ , 41.18 ;  $\text{SO}_3$ , 58.82 ; *crystallized as gypsum* ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = 172$ ) ; *Sp. Gr.* 2.30 ; *water in 100 parts*, 20.93.—This compound occurs free from water in the mineral *anhydrite*, crystallized in rectangular prisms, which are found in the salt rocks of the Tyrol, and in Upper Austria ; but it is much more abundant as a hydrate with  $2\text{H}_2\text{O}$  : it is then met with either in transparent flattened prisms, known as *selenite*, or still more frequently in a fibrous, granular, compact, or earthy form, constituting the different varieties of *gypsum* and *alabaster*. Calcic sulphate is a very common impurity in spring water. The solubility of calcic sulphate diminishes as the temperature rises : at ordinary temperatures water is able to dissolve about 150 grs. per gallon, or 2.142 grms. per litre ; but, according to Chandler, at a temperature of  $255^{\circ} \cdot 2$  ( $124^{\circ}$  C.), when the pressure is equal to that of about two atmospheres of steam, little more than one-fourth of this amount is held in solution ; while under a pressure of three atmospheres, or at  $271^{\circ} \cdot 4$  ( $133^{\circ}$  C.), not more than one-twentieth is soluble, and at a temperature of  $302^{\circ}$  ( $150^{\circ}$  C.) it is practically insoluble. Chlorides of calcium and magnesium diminish the solubility of calcic sulphate, while sodic hyposulphite is said to increase it tenfold. Waters which contain calcic sulphate in solution are often termed *selenitic* ; they deposit

upon the interior of boilers in which they are used, a strongly adherent fur or crust, the composition of which is  $2(\text{CaSO}_4) \cdot \text{H}_2\text{O}$ .

Calcic sulphate is produced whenever a strong solution of a calcium salt is precipitated by any sulphate, in which case it falls as a white voluminous sparingly soluble hydrate. It is insoluble in alcohol, but is dissolved to some extent by diluted nitric and hydrochloric acids. When heated it loses its water, and if the temperature be raised to bright redness, the anhydrous mass fuses, and may be obtained in crystals the same in form as those of anhydrite.

Gypsum constitutes a manure of considerable utility when judiciously employed; but the most remarkable property of calcic sulphate, and that for which it is chiefly valued, is the power which the hydrated variety possesses, after it has been deprived of water by a heat not exceeding  $500^\circ$  ( $260^\circ$  C.), of again combining with water, and binding or setting into a hard mass. The friable mass obtained by depriving gypsum of water and reducing it to a fine powder constitutes what is known as *plaster of Paris*, from the circumstance that it is manufactured abundantly in the vicinity of the French metropolis. If the dry powder be made into a thin paste with water, the mixture becomes solid in a few minutes, expands perceptibly at the moment of solidification, and experiences a considerable rise of temperature, which in large masses may amount to  $25^\circ$  or  $30^\circ$  C.: a combination of 2 atoms of water with 1 atom of calcic sulphate occurs, and eventually it becomes as hard as the original gypsum, each atom of the salt recombining with the 2 atoms of water it had lost. It is, however, particularly worthy of observation, that if the sulphate be heated to redness, it becomes very much denser, assumes a crystalline structure, and loses the power of setting or solidifying when mixed with water.

Plaster of Paris is manufactured in large quantities for architectural purposes: it is also extensively used in modelling, and in taking accurate copies of objects of every description. Suppose, for instance, it were desired to copy a medal: a raised rim of pasteboard is attached to the medal, which is anointed with a little oil, to prevent the plaster from adhering to its surface. The dried plaster is then mixed with water till it is of the consistence of thin cream, and is immediately applied carefully with a hair pencil to every part of the surface, so as to exclude air; after which a thicker cream is poured into the mould: in a few minutes the mass becomes solid, and the cast may be removed from the medal.

The addition of 1 or 2 per cent. of many salts—particularly of alum, of potassic sulphate, or of borax—confers upon gypsum some properties of considerable practical importance. Gypsum which has been thus treated will endure a dull red heat without losing its power of setting when mixed with water. It becomes much denser than ordinary plaster, and, when mixed with water, sets in

the course of a few hours, and forms a hard material which takes a high polish. Keene's, Martin's, and Keating's cement are the respective names under which plaster so treated is known. *Stucco* consists of coloured plaster, mixed with a solution of size. The different colours exhibited by stucco are obtained by the admixture of oxides of iron and other metals. By friction its surface is susceptible of a high polish.

*Polyhallite* is the mineralogical name for the sulphate of potassium magnesium and calcium ( $K_2Ca_2Mg_4SO_4 \cdot 2H_2O$ ), which is sometimes found native associated with rock-salt, as at Stassfurt, and has been formed occasionally during the manufacture of tartaric acid. It is decomposed by water.

Calcic sulphate also forms a double salt with sodic sulphate, which occurs native under the name of *glauuberite* ( $Na_2Ca_2SO_4$ ); it is anhydrous, and nearly insoluble in water.

(653) CALCIC NITRATE, or *Nitrate of calcium* ( $Ca_2NO_3 \cdot 4H_2O$  = 164 + 72: *Sp. Gr. anhydrous*, 2.24; *cryst.* 1.780) is a deliquescent salt, which crystallizes in long prisms: when anhydrous, it emits light if gently heated. It is soluble in alcohol.

(654) CALCIC CARBONATE, or CARBONATE OF LIME ( $CaCO_3$ , = 100): *Sp. Gr. of Iceland spar*, 2.72; *of Aragonite*, 2.97; *Comp. in 100 parts*, CaO, 56;  $CO_2$ , 44.—This substance is one of the most abundant components of rocks and minerals. In the uncrystallized condition, it forms the different varieties of *limestone*, *oölite*, *chalk*, and *calcareous marl*; it is the principal constituent of corals, of the shells of fishes, and of the eggshells of birds; it also enters in greater or less quantity into the bones of animals. In minute granular crystals it forms the different kinds of *marble*, and it is found in a greater variety of regular crystalline forms than any other known compound. Its primary form is a rhombohedron, as is seen in *Iceland spar*, but it also occurs in the incompatible form of *aragonite*, in six-sided prisms, and is consequently dimorphous. Aragonite is isomorphous with strontic carbonate, and its crystals not unfrequently contain small quantities of this mineral, the occurrence of which it is supposed may assist in determining the assumption of the prismatic form by the calcic carbonate. When aragonite is heated it falls to powder, and the grains are stated to assume the form of minute rhombs. Calcic carbonate is produced whenever a calcium salt is precipitated by the addition of an alkaline carbonate, and if the solutions be mixed at the boiling-point, the carbonate falls in microscopic crystals, having the form of aragonite.

It is sometimes necessary to obtain a perfectly pure calcic carbonate; for this purpose a solution of calcic nitrate may be mixed with an excess of lime-water, which precipitates magnesia, alumina, ferric oxide, and other metallic oxides; the filtered solution is decomposed by the addition of a mixture of ammonia

and ammoniac sesquicarbonate; the precipitate is washed thoroughly, then dried, and heated to low redness.

Calcic carbonate is decomposed by a red heat, if the gas can freely escape; but, according to Sir J. Hall, in closed vessels it fuses without undergoing decomposition, and on cooling becomes converted into a granular crystalline mass, like marble.

A combination of calcic and sodic carbonates, insoluble in water, was found at Merida, in South America, and called *Gay-Lussite* ( $\text{CaNa}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$ ). *Barytocalcite* ( $\text{CaBa}_2\text{CO}_3$ ) is a native double carbonate of calcium and barium, which crystallizes in oblique prisms.

(655) *Calcareous Waters*.—Calcic carbonate is soluble in pure water to the extent of about 0.3 mgrm. per litre, or rather more than 2 grains in 1 gallon, but it is freely taken up by water charged with carbonic acid, and is deposited again in anhydrous crystals as the gas escapes. In this way enormous masses of crystallized calcic carbonate are formed. In the limestone hills of Derbyshire, and in various other localities, caverns occur in which this phenomenon is perpetually exhibited; water charged with carbonic acid and calcic carbonate makes its way through the roof of the cavern, where, as the carbonic acid gradually escapes, the carbonate is deposited in dependent masses, like icicles, termed *stalactites*; whilst the water falling on the floor of the cavern before it has parted with all its excess of carbonic acid and dissolved limestone, deposits a fresh portion of the crystalline matter; and thus a new growth, or *stalagmite*, gradually rises up to meet the stalactite which depends from the roof: in this way a natural pillar of crystallized calcic carbonate is formed.

It is in a similar manner that the calcareous deposits from the lakes of volcanic districts are produced. These deposits, when porous, have received the name of *tufa*; when more compact, they are termed *travertine*. Travertine is formed abundantly in many of the Italian lakes; it was highly valued for architectural purposes by the Romans, as it is a material easily wrought, may be polished readily, and possesses great durability and beauty.

Many spring waters contain calcic carbonate held in solution by carbonic acid: when the water is boiled this acid is expelled, and the carbonate is deposited, forming a lining more or less coherent upon the sides of the vessel. In steam boilers this becomes a serious evil: it is effectually prevented by the addition of a small quantity of soda-ash or of sal ammoniac to the water; in the latter case ammoniac carbonate is formed, and volatilized, while calcic chloride remains dissolved.

Dr. T. Clark has contrived a plan for softening such calcareous waters, by removing the carbonic acid from them, and causing



the precipitation of the calcic carbonate by thus depriving it of its solvent. This method consists essentially in the addition of milk of lime to such waters, until the water gives a very faint brown tinge on testing it with a solution of argentic nitrate: this reaction indicates that a slight excess of lime has been added, which occasions a precipitate of brown hydrated argentic oxide. In this operation the lime combines with the excess of carbonic acid in the water: the calcic carbonate thus formed, being insoluble, is precipitated along with a portion of calcic carbonate previously held in solution by the carbonic acid. After the lapse of twenty-four hours the water becomes perfectly bright and clear. If colouring or organic matters be present in the water, a considerable portion of both goes down with the chalk. In applying this process upon a large scale, it is found advantageous to add a slight excess of lime in the first instance, and afterwards to destroy this excess by a fresh addition of unlimed water. The carbonate is then separated in granular crystals, which speedily subside. These crystals are formed much more slowly if the lime be not first in slight excess.

Dr. Clark has introduced a method of testing the hardness of waters by the application of the *Soap-test*, which has been extensively used. The operation may be conducted in the following manner:—

A solution of soap in proof spirit (containing about 120 grains of curd soap to the gallon) is first prepared. In order to graduate this solution, 16 grains of Iceland spar, or Carrara marble, are dissolved in a flask in pure hydrochloric acid, evaporated to dryness in the flask, redissolved in water, and a second time evaporated to dryness. On again dissolving it in water, a perfectly neutral solution of calcic chloride is obtained; this solution is then diluted with distilled water until it measures 1 gallon. It will now represent a water of  $16^{\circ}$  of hardness; that is to say, it will correspond in hardness to a water containing 16 grains of calcic carbonate per gallon, each degree of hardness upon Clark's scale representing an amount of any calcium salt corresponding to 1 grain of chalk per gallon in the water. 1000 water-grain measures of this solution are next transferred by a pipette, graduated to deliver exactly this quantity, into a bottle which will hold 5 ounces, and accurately fitted with a glass stopper. The soap solution is then added to the water from a burette, each division of which corresponds to 10 water-grains. After each addition of the soap-test, the stopper is replaced in the bottle, and the bottle is briskly shaken for a minute, after which it is laid upon its side; fresh portions of the soap being added in small quantities until a fine lather in uniform small bubbles remains unbroken over the surface for three minutes. The number of measures of the soap-test employed is noted, and the strength of the solution is increased or diminished by the addition of soap or of spirit, as may be necessary, until exactly 32 measures are required for 1000 water-grains of the standard solution of  $16^{\circ}$  of hardness. After the solution has been made up to this strength, the experiment is repeated, in order to ascertain that the adjustment is correct.

In applying the test, 1000 measured grains of the water to be examined are introduced into the stoppered bottle, and the operation is proceeded with as above directed, reading off the number of test-measures required, in order to produce a

permanent lather. The degree of hardness of the water is then obtained by simple inspection of the subjoined table. The results are, however, apt to be inaccurate, if large quantities of magnesian salts are present. (D. Campbell, *Phil. Mag.* 1850, xxxvii. 171.) Sometimes the water exceeds  $16^{\circ}$  in hardness; in that case it should be diluted with an equal measure, or, if necessary, with twice, or even with thrice its bulk of distilled water. 1000 grain-measures of the diluted water are then to be tested as usual, and the number of divisions of the soap-test employed is to be read off, and the degree of hardness corresponding to it is noted from the table. This degree must be finally multiplied by 2, by 3, or by 4, according to the extent to which the water had been previously diluted.

*Clark's Table of Hardness of Water.*

Degree of hardness.		Measures of soap-test.				Diff. for the next 1° of hardness.
0	(Distilled water)	1'4				1'8
1	...	3'2	...	...	...	2'2
2	...	5'4	...	...	...	2'2
3	...	7'6	...	...	...	2'0
4	...	9'6	...	...	...	2'0
5	...	11'6	...	...	...	2'0
6	...	13'6	...	...	...	2'0
7	...	15'6	...	...	...	1'9
8	...	17'5	...	...	...	1'9
9	...	19'4	...	...	...	1'9
10	...	21'3	...	...	...	1'8
11	...	23'1	...	...	...	1'8
12	...	24'9	...	...	...	1'8
13	...	26'7	...	...	...	1'8
14	...	28'5	...	...	...	1'8
15	...	30'3	...	...	...	1'7
16	...	32'0	...	...	...	

(656) *Building Materials*.—Calcic carbonate forms the basis of some of the materials most highly prized for building purposes, besides furnishing the costly varieties of marble used for interiors. The oölites, such as those from the Isle of Portland and the neighbourhood of Bath, resist the weather admirably; they admit of being readily fitted and cut, and yet possess considerable hardness. Many shelly limestones are also well adapted for these purposes. Where elaborate carving is required, a well-crystallized magnesian limestone (or double carbonate of calcium and magnesium), such as that employed in the new Houses of Parliament, is preferred; it is very close and compact, sufficiently soft to be easily sculptured, but retains a sharp outline.

Many fine-grained, porous, calcareous and magnesian stones have the inconvenience of splitting into flakes after a few years' exposure; this generally occurs from the absorption of water, and its expansion when the moisture thus absorbed becomes frozen during winter. A simple and ingenious mode of ascertaining whether a building stone is liable to this defect was invented by Brard:—It consists in taking a smoothly cut block of the stone, 3 or 5 centim. or one or two inches in the side, and placing it in a cold saturated solution of sodic sulphate. The temperature of the solution is gradually raised to the boiling-point, it is

allowed to boil for half an hour, and then the stone is left to cool in the liquid. When cold, it is suspended over a dish, and once a day for a week or a fortnight plunged for a few moments into a cold saturated solution of sodic sulphate, and is then again freely suspended in the air. The sulphate crystallizes in the pores of the stone, and splits off fragments of it. A similar experiment is made upon an equal sized mass of stone which is known to be free from this defect. By the comparative weight of these fragments in the two cases the tendency of the stone to the defect in question may be estimated.

A stone which is placed in a building conformably to its position in the quarry, so that its seams shall lie horizontally, is much less liable to injury from the weather than where this point is neglected.

In the selection of a building-stone, regard must be had not merely to its durability, but also to the locality in which it is to be placed. A stone which, like a magnesian limestone, may endure unchanged for ages in the open country air, may yet in the atmosphere of a large city become rapidly disintegrated, owing to the action of the sulphuric acid produced by the immense quantities of coal which are burned. Decay from this cause is strikingly shown in the stone used in London in some parts of the new Houses of Parliament, and still more so in the new buildings in Lincoln's Inn.

A valuable report upon the composition and quality of various kinds of building stones was made to the British Government in 1839, upon the occasion of the rebuilding of the Houses of Parliament.

The other varieties of building stones are mostly siliceous. To this class belong all the sandstones, which consist chiefly of grains of silica united by a cement more or less ferruginous. The durability of the stone depends mainly upon the character of this uniting material. Many igneous rocks, such as porphyry, basalt, and more especially granite, are also used for building purposes; but from their hardness, they are seldom wrought, except when, as in quays, bridges, or causeways, the constant wear is unusually great, and where softer though less expensive materials would soon be destroyed.

(657) **CALCIC PHOSPHATES.**—The most remarkable of the *calcic phosphates* is that known as the *bone phosphate* ( $\text{Ca}_4\text{H}_3\text{PO}_4$ ), so named from its forming the principal earthy constituent of the animal skeleton. (*Comp. in 100 parts, after ignition, CaO, 51.26; P<sub>2</sub>O<sub>5</sub>, 48.74, Berzelius.*) It is easily procured by adding a solution of calcic chloride, drop by drop, to a solution of hydrodisodic phosphate in excess, when it falls as a gelatinous precipitate with  $2\text{H}_2\text{O}$ . It may also be obtained from calcined bones by digesting them in nitric acid, and precipitating the filtered solution by caustic ammonia. This phosphate is insoluble in

water, but is readily dissolved by acetic, and the stronger acids. It occurs native as a white amorphous mineral, known under the name of *phosphorite*. In the Norfolk crag considerable deposits of brown rounded pebbles occur, known under the name of *coprolites*, from the erroneous supposition that they were the fossilized dung (κόπρος) of extinct animals: they contain a large proportion of calcic phosphate mixed with calcic carbonate and fluoride. In the green-sand formation near Farnham, and in other localities, nodules chiefly composed of calcic phosphate are also found abundantly.

A true tricalcic diphosphate occurs naturally crystallized in hexagonal prisms, which, when colourless, are called *apatite*; when of a green colour it is termed *morozite*; in these minerals three atoms of the phosphate are associated with one atom of calcic chloride and fluoride:  $3(\text{Ca}_3\text{2PO}_4), \text{Ca}(\text{ClF})_2$ . If bone-ash be fused with about 4 times its weight of sodic chloride, and allowed to cool very slowly, delicate crystals having the form of apatite are found lining the cavities contained in the mass (Forchhammer). When hydrodisodic phosphate in solution is added drop by drop to an excess of calcic chloride, a semi-crystalline precipitate falls, which, according to Berzelius, consists of  $(2\text{Ca}''\text{HPO}_4, 3\text{H}_2\text{O})$ , and the liquid becomes acid.

Several other calcic phosphates may be formed, corresponding in composition to the various sodic phosphates. The soluble acid phosphate, or *superphosphate of lime*  $(\text{Ca}''\text{H}_2\text{2PO}_4)$ , is prepared by treating bone-earth with two-thirds of its weight of oil of vitriol, as in the preliminary stage of the extraction of phosphorus. It is largely manufactured as a manure for turnips.

(658) A double *Borate of calcium and sodium*, or *Boro-natro-calcite*  $[2(\text{NaCa}''3\text{BO}_3), 3\text{B}_2\text{O}_3, 18\text{H}_2\text{O}]$ , is found at Iquique, in Peru, in the form of rounded nodules, composed of fine silky needles. It is but sparingly soluble in hot water, to which it communicates an alkaline reaction; but it is easily dissolved by diluted acids. This mineral has recently been imported into this country to some extent for the preparation of borax, which is easily obtained from it by dissolving the compound in hot diluted hydrochloric acid, and precipitating the calcium as carbonate by the addition of sodic carbonate; the clear, supernatant liquid on evaporation yields crystals of borax, whilst sodic chloride remains in solution.

(659) **CHARACTERS OF THE CALCIUM SALTS.**—The calcium salts are colourless. They give no precipitate with *ammonia*, but yield a white precipitate of calcic carbonate, with the *carbonates of the alkali-metals*. Solution of *calcic sulphate* produces no precipitate; the calcium salts are thus distinguished from those of barium and strontium: they yield no precipitate with *ammonic*

*hydrosulphide.* *Ammonic oxalate*, even in very dilute neutral or alkaline solutions of salts of calcium, throws down a white calcic oxalate, which is soluble in nitric and hydrochloric acids, but not in acetic acid. Calcic salts give a greenish-yellow tinge to flame, and when examined by the spectroscope may be recognized by a bright line in the orange, and a broad rather less luminous band in the green; fainter lines are also visible in the red; and occasionally a bright blue band is seen.

*Estimation of Calcium.*—In the determination of calcium for analytical purposes the oxalate is the precipitate usually employed; but before weighing it is heated to dull redness, so as to convert the calcic oxalate into carbonate: 100 parts of the carbonate represent 56 of lime: if heated for a few minutes to a bright red, quicklime is obtained. If no other base be present, calcium may also be estimated in the form of sulphate. If the calcium be not already in the state of sulphate, the salt is heated with an excess of sulphuric acid, and ignited; when cold, it is weighed: 100 grains of calcic sulphate represent 41·18 of lime.

Magnesium will be described in the group containing zinc and cadmium (683 *et seq.*).

## CHAPTER XIV.

### GROUP III.—METALS OF THE EARTHS.

§ I. ALUMINUM: ( $Al''' = 27\cdot5$ ). *Sp. Gr. from 2·5 to 2·67.*  
*Sp. Heat, 0·2143. Electric Conductivity at 68° (20° C.),*  
*33·76. Atomic Vol. solid, 10·56.*

(660) THE pure earths are white, insipid, insoluble compounds, the oxides of metals which possess a high attraction for oxygen. A single oxide only of each metal of this class is known.

Of these metals the most abundant and important is ALUMINUM, which derives its name from alum, into the composition of which it enters. Indeed, alumina (the oxide of aluminum) constitutes about 10 per cent. of this salt.

*Preparation.*—1. Aluminum was originally procured by Wöhler, by decomposing aluminic chloride in a porcelain or platinum tube by means of potassium. He obtained it first as a steel-grey powder, and subsequently in malleable globules. In the pulverulent form it is gradually oxidized by boiling water, and more rapidly by alkaline solutions. When heated in this form in oxygen gas, it takes fire and burns with a vivid light, emitting so intense a heat as to fuse the alumina, which forms a yellowish mass, in colour and hardness resembling native crystallized alumina as it exists in corundum.

2.—Bunsen obtains aluminum by the electrolytic decomposition of the double chloride of sodium and aluminum ( $\text{NaCl}, \text{AlCl}_3$ ). This salt melts at about  $392^\circ$  ( $200^\circ \text{C.}$ ), and readily furnishes aluminum by a process similar to that adopted in the case of magnesium (683) : but as the aluminum is heavier than the fused salt, it is more easily collected than magnesium.

3.—Aluminum may be prepared in the laboratory, by the method of Deville (*Ann. de Chimie*, III. xliii. 5).—Into a wide tube of hard glass of an inch or an inch and a half (from 25 to 40<sup>mm.</sup>) in diameter, about half a pound (250 grms.) of dry aluminic chloride is introduced, and kept in its place by plugs of asbestos ; a current of dry hydrogen, perfectly free from air, is transmitted, and the chloride is very gently heated ; in this way traces of hydrochloric acid and chlorides of sulphur and silicon are expelled. Three or four small porcelain trays, each containing 40 or 50 grains (about 3 grammes) of sodium, freed from adhering naphtha by pressure between folds of blotting-paper, are then introduced into the tube ; the current of hydrogen is still maintained, and heat is applied to the part of the tube which contains the sodium. This end of the tube must be slightly elevated, in order to prevent the melted aluminic chloride from running down upon the sodium ; in which case the heat emitted is so intense as to crack the tube. When the sodium is melted, the aluminic chloride is gradually distilled over by the application of a regulated heat, and is reduced with vivid incandescence. The aluminum is condensed in the porcelain trays, in which also a sodio-aluminic chloride collects around the reduced aluminum. These trays and their contents when cold are withdrawn from the glass tube, and placed in a porcelain tube through which a current of hydrogen is transmitted, whilst the tube is raised to a bright red heat ; the aluminum fuses into globules in the porcelain trays ; and by fusing it once more in a porcelain crucible under a layer of the sodio-aluminic chloride, a button of pure aluminum is obtained.

Messrs. Bell of Newcastle have carried out the process of Deville as a manufacturing operation. They prepare a trisodic aluminate ( $3\text{Na}_2\text{O}, \text{Al}_2\text{O}_3$ ) from Bauxite, an aluminous ore of iron nearly free from silica (663), and precipitate the alumina as hydrate, by means of carbonic or of hydrochloric acid. The precipitated aluminic hydrate is then mixed with common salt and charcoal, made into balls of the size of an orange, and dried. These balls are placed in vertical earthen retorts heated to redness, and through them dried chlorine is transmitted. The sodio-aluminic chloride ( $\text{NaCl}, \text{AlCl}_3$ ) distils over. Ten parts of this double salt and 5 of cryolite or fluor-spar are thrown with 2 parts of sodium into a reverberatory furnace, previously heated strongly ; the damper is then closed. An intense reaction, attended with great evolution of heat, occurs, and the aluminum collects at the bottom in a melted form, while the chlorine is removed by combination with the sodium.

4.—Rose obtains aluminum from cryolite ( $3\text{NaF}, \text{AlF}_3$ ) by fusing it with sodium. For this purpose Wöhler recommends 7 parts of sodic chloride to be melted with 9 of potassic chloride, and the mass thus furnished to be finely powdered and intimately mixed with its own weight of cryolite in fine powder. This

powder is to be introduced with a fifth or a sixth of its weight of sodium (arranged in alternate layers of the powder and the metal), into a dry earthen crucible, which is to be heated rapidly in a wind furnace. An intense reaction occurs, and a portion of the sodium burns off. The mixture is afterwards heated for about a quarter of an hour until it is in liquid fusion, and is then allowed to cool. The aluminum generally collects at the bottom into a well-formed button, which is frequently crystalline on its surface. In some experiments the quantity of reduced metal amounted to one-third of the proportion present in the mineral employed.

(661) *Properties*.—As prepared by Deville's process, aluminum is a white malleable metal, nearly resembling zinc in colour and hardness: it may be rolled into very thin foil, and admits of being drawn into fine wire; after it has been rolled, it becomes much harder and more elastic. It conducts electricity with about one-third the power of silver. Aluminum is remarkably sonorous, and emits a clear musical sound when struck with a hard body. Fused aluminum crystallizes readily as it cools, apparently in regular octohedra; its point of fusion is below that of silver: when melted it may be readily cast in moulds of metal or of sand. It may be heated intensely in a current of air in a muffle without undergoing more than a superficial oxidation, and it is but slowly oxidized when heated to full redness in an atmosphere of steam. When heated in the form of foil with a splinter of wood in a current of oxygen it burns with a brilliant bluish-white light. Aluminum shows no tendency to volatilize, either when heated intensely in closed vessels or when subjected to a succession of electric sparks.

Nitric acid, whether concentrated or diluted, is without action upon aluminum at the ordinary temperature, and dissolves it very slowly even when boiled upon the metal. Hydrochloric acid, on the contrary, both when concentrated and when diluted, attacks it rapidly, forming aluminic chloride, whilst hydrogen is disengaged. Solutions of the alkalies, especially when aided by heat, also attack aluminum with energy, producing alumina, which is dissolved by the alkaline solution, whilst hydrogen gas is liberated. From its lightness and inalterability in the air, aluminum has been applied to the preparation of small weights: but some difficulty was at first experienced in working the metal for want of a suitable solder. The solder now generally preferred is an alloy of 4 parts of copper, 6 of aluminum, and 90 of zinc. No flux is used, and it is proposed to employ small soldering tools of aluminum. The metal is chiefly used for ornamental articles.

Aluminum readily forms alloys with copper, silver, and iron, but it may be melted with lead without any combination between the two metals taking place. Its alloys with copper are very hard, and susceptible of a high polish; they vary in colour from white to golden yellow, according to the proportion of the two metals: one of these ( $\text{Cu}_3\text{Al}$ ), a beautiful alloy of a golden yellow colour, containing about 10 per cent. of aluminum, is manufactured by Messrs. Bell under the name of *aluminum bronze*: it is well fitted for castings, and possesses great tenacity and hardness. For the preparation of this alloy copper of high purity is needed. Aluminum also combines readily with carbon and silicon, forming greyish, granular, brittle, and crystalline compounds, which present a considerable analogy to cast iron. It does not combine with mercury.

Finely divided aluminum burns brilliantly in the vapour of sulphur, and forms a black sesquisulphide ( $\text{Al}_2\text{S}_3$ ), of semi-metallic appearance, which is rapidly decomposed by water, with formation of hydrated alumina and sulphuretted hydrogen.

(662) ALUMINA ( $\text{Al}_2\text{O}_3=103$ ); *Sp. Gr. of ruby*, 3.95; *Comp. in 100 parts*, Al, 53.39; O, 46.61.—This is the only known oxide of aluminum: from its isomorphism with the sesquioxide of iron, and its general resemblance to it in properties, it is regarded as a sesquioxide. It forms one of the materials that enter most largely into the composition of the superficial strata of the earth. It is the basis of all the varieties of clay, and is present in greater or less quantity in almost every soil. Alumina occurs nearly pure, and crystallized in six-sided prisms, in *corundum*, in which mineral it has a specific gravity of 3.95, and is hard enough to cut glass. The *sapphire* and the *ruby* are also composed of this earth, tinged with a small quantity of oxide of chromium. They are only inferior to the diamond in hardness. *Emery*, which from its hardness is so largely used in grinding and polishing, after it has been powdered and levigated, is another form of alumina, coloured with oxides of iron and manganese.

In order to obtain alumina, it is sufficient to ignite pure ammonia alum ( $\text{H}_4\text{NAl}'''2\text{SO}_4.12\text{H}_2\text{O}$ ) intensely for some time: the water, ammonia, and sulphuric acid are expelled, and anhydrous alumina is left, in the proportion of 11.34 parts of alumina to 100 of the crystallized salt. It is, however, nearly impossible to drive off the last portions of sulphuric acid, as the salt swells up enormously, and forms a white, porous, infusible mass, which is an extremely bad conductor of heat. Alumina may also be procured by precipitation from alum quite free from iron; the



salt should be dissolved in water and decomposed by potassic carbonate in slight excess : the liquid should be warmed, and the precipitate well washed ; but since traces of potash always adhere to it obstinately, it must be redissolved in hydrochloric acid, and then thrown down by ammonia or ammoniac carbonate : in which case it falls as a white, semitransparent, bulky, gelatinous hydrate, which must be again thoroughly washed. In this form alumina is completely soluble in a solution of potash, and is readily taken up by acids. On drying, it contracts very much, and forms a yellowish translucent mass, like gum, retaining  $3\text{H}_2\text{O}$ . *Diaspore* is a natural hydrate ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), which decrepitates strongly when heated, and falls to powder. Alumina may also be obtained from trisodic aluminate (663) by adding hydrochloric acid in quantity just sufficient to form sodic chloride.

Aluminic hydrate when ignited loses its water, and at a certain temperature presents an appearance of sudden incandescence ; it contracts greatly at the moment that this effect is produced, and is afterwards nearly insoluble in acids. Hydrated alumina is strongly hygroscopic, and adheres to the tongue when applied to it.

Alumina fuses before the oxyhydrogen blowpipe, and yields a colourless, transparent mass, resembling corundum. Gaudin states that artificial crystals, having the form and hardness of the ruby, may be obtained by calcining equal parts of potassic sulphate and alum, and introducing the mixture in fine powder into a crucible lined with lampblack. The cover is then to be luted on, and the crucible exposed to the highest heat of a forge for a quarter of an hour. In this operation the sulphuric acid of the aluminic sulphate is expelled, the potassic sulphate is reduced to dipotassic sulphide, and this compound dissolves a portion of the liberated alumina, depositing it in minute prismatic colourless crystals, during the slow cooling of the mass. These crystals may be cleansed from adhering impurities by digestion in dilute aqua regia. Similar minute crystals have also been obtained by Deville, who has succeeded in imitating the hue both of the ruby and the sapphire. Alumina forms salts with the more powerful acids, but these salts are readily decomposed : they all have an acid reaction ; and indeed alumina possesses properties which approach somewhat to those of an acid, for it has a strong tendency to unite with basic oxides. The *spinelle ruby*, for example, is a native magnesian aluminate ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ), and *gahnite* is a zincic aluminate ( $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ ). Fremy has also obtained a white granular compound of alumina with potash, to which he assigns a compo-

sition corresponding with the formula ( $K_2O, Al_2O_3$ ). When the solution of alumina in potash or soda is exposed to the air it absorbs carbonic acid, and an aluminic trihydrate is deposited in regular crystals.

Alumina when combined with silica forms clay, which is the basis of porcelain and of earthenware. To the dyer and the calico-printer the compounds of alumina are of high value: hydrated alumina has the property of combining intimately with certain kinds of organic matter, and when aluminic salts are mingled with coloured vegetable or animal solutions, and precipitated by the addition of an alkali, the alumina carries down the greater portion of the colouring matter, forming a species of pigments termed *lakes*. By soaking the cloth with a preparation of alumina, the earth attaches itself to the fibre; and if cloth thus prepared be plunged into a bath of the colouring matter, it becomes permanently dyed. Most colouring matters would be removed by washing, were it not for the intervention of some *mordant*, or substance which thus adheres to the fibre as well as to the colouring matter. Stannic oxide, and ferric and chromic oxides, resemble alumina in this respect, and are largely used as mordants in dyeing calicoes and woollens.

Mr. Crum (*Q. J. Chem. Soc.* vi. 216) has described a remarkable modification of hydrated alumina, which, in the presence of a very small proportion of acetic acid, is largely soluble in water, and is coagulated and rendered insoluble by a minute trace of sulphuric acid. It appears from the experiments of Péan de St. Gilles (*Ann. de Chimie*, III. xlv. 47) that ferric oxide admits of a similar modification: these compounds will be further alluded to when the salts of acetic acid are described: various other soluble colloidal oxides have been lately described by Graham (*Phil. Trans.* 1861, and *Proceed. Roy. Soc.* 1864).

(663) *Trisodic aluminate*, or *Aluminate of sodium* ( $Na_3AlO_3$ ).—This compound now forms an article of commerce. It is obtained by heating Bauxite, a hydrated aluminous ferric oxide, which contains from 60 to 75 per cent. of alumina, and only from 1 to 3 per cent. of silica. This ore is mixed in fine powder with sodic carbonate or soda-ash, and heated to bright redness, until no effervescence occurs on the addition of an acid. On lixiviation, the aluminate is dissolved out and separated, by filtration into a vessel, from which, to accelerate the operation, the air is exhausted. The filtrate when evaporated to dryness gives a whitish, infusible, but freely soluble compound, which furnishes a valuable material in the preparation of lakes for pigments, as well as for the purposes of a mordant to the calico-printer, which will probably to a large extent supersede the use of the different forms

of alum. The silica remains behind in the form of an insoluble sodic alumino-silicate.

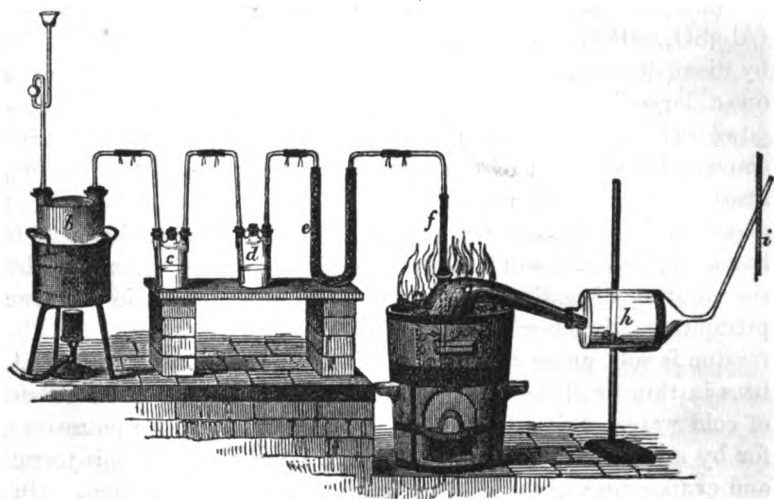
If a solution of trisodic aluminate is exposed to the action of a current of carbonic acid, sodic carbonate is produced, and hydrated alumina precipitated contaminated with soda. If hydrochloric acid in quantity sufficient to neutralize the soda be added to a solution of the aluminate, the alumina is precipitated in a form in which it may be washed; but the precipitate is simply dried when it is to be used in the preparation of aluminum, for which it is chiefly required; the presence of sodic chloride being advantageous in the subsequent operations. A curious reaction occurs when solutions of trisodic aluminate and aluminic chloride are mixed in equivalent proportions; sodic chloride is formed, and the alumina from both compounds is precipitated in the form of hydrate;  $2(\text{Na}_3\text{AlO}_3) + \text{Al}_2\text{Cl}_6 = 2\text{Al}_2\text{O}_3 + 6\text{NaCl}$ .

(664) ALUMINIC CHLORIDE, or *Chloride of aluminum* ( $\text{Al}_2\text{Cl}_6$ , =268); *Sp. Gr. of Vapour*, 9.32; *Mol. Vol.*  ; *Rel. wt.* 134. — The anhydrous chloride cannot be formed directly by dissolving alumina in hydrochloric acid, and evaporating to dryness; since during the expulsion of the water, a great part of the acid is also driven off. It may be procured as a yellow, anhydrous, volatile sublimate, by a process devised by Oersted:—alumina, mixed with charcoal powder, is made up into paste with starch or oil, and subdivided into pellets: these pellets are charred in a covered crucible, and then exposed to ignition in a current of dry chlorine. In this operation, carbon, in a very finely divided state, is mixed with the alumina; when the mass is heated with chlorine, the carbon unites with the oxygen of the alumina, and the chlorine seizes the liberated aluminum;  $\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 = \text{Al}_2\text{Cl}_6 + 3\text{CO}$ . Aluminic chloride condenses in the cool part of the tube in a crystalline, somewhat translucent mass, or as an amorphous powder.

In preparing this chloride in the laboratory, an apparatus similar to that shown in fig. 349 may be used: *b* is a vessel containing a mixture of black oxide of manganese and hydrochloric acid, for generating chlorine; *a* is a water-jacket, for applying a moderate heat; *c* is a wash-bottle containing water; *d* contains strong sulphuric acid; *e* is a bent tube filled with pumice-stone soaked with oil of vitriol, to remove the last traces of moisture; *g* is an earthen retort filled with the mixture of charcoal and alumina, heated by a charcoal fire. The chlorine is conveyed nearly to the bottom of this retort by means of a porcelain tube, *f*, luted into the tubulure: the gas reacts upon the mixture in the retort, forming carbonic oxide and aluminic chloride; the chloride condenses in the gas-jar, *h*, which is placed for its reception: the open mouth of this jar is closed by means of a funnel, luted on with a strip of pasted paper; and the carbonic oxide escapes through the open tube, *i*, into the chimney. In order to purify crude aluminic chloride from the small quantity of volatile ferric chloride

which usually accompanies it, the compound is redistilled from iron wire, by which the ferric chloride is converted into the much less volatile ferrous chloride, and the aluminic chloride sublimes nearly in a state of purity.

FIG. 349.



Deville prepares this chloride on a large scale from a mixture of coal tar and alumina, which is heated first in iron pots till the vapours of tar cease to escape, and then in a clay retort, such as is used in gas making, but set vertically; a current of chlorine is sent over the ignited mass, and the product of the operation is received in a chamber lined with glazed brickwork. (See also par. 660.)

If aluminic chloride be heated in considerable mass, it melts at a dull red heat, and near its fusing-point sublimes rapidly; when exposed to the air it emits fumes of hydrochloric acid: it is soluble in alcohol, is very deliquescent, and when thrown into water hisses from the heat developed by the violence of the combination. The aqueous solution, when concentrated by a very moderate heat, yields crystals with the formula  $\text{Al}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ . By subliming the anhydrous chloride in a current of sulphuretted hydrogen it forms a combination with this gas: this compound is decomposed by resublimation, or by solution in water. The chloride may also be made to combine with phosphuretted hydrogen, and with ammonia.

*Aluminic bromide* ( $\text{Al}_2\text{Br}_6=535$ ; *Mol. Vol.*  ; *Rel. wt.* 267·5; *Sp. Gr. Vapour*, 18·6) and *iodide* ( $\text{Al}_2\text{I}_6=817$ ; *Mol. Vol.*  ; *Rel. wt.* 408·5; *Sp. Gr. Vapour*, 28·227) have also been obtained.

(665) **ALUMINIC FLUORIDE** occurs native, combined with sodic fluoride, forming *cryolite* ( $3\text{NaF} \cdot \text{AlF}_3$ ). It is found in large quantity in Greenland, and as it is easily decomposed by sodium, it has been employed as a source of

metallic aluminum, of which it contains 13 per cent. Another highly prized aluminous mineral, containing fluorine, is the *topaz*. It is extremely hard; the colourless variety has a lustre which has sometimes caused it to be mistaken for the diamond. Its composition may be represented by the formula  $[2(\text{Al}_2\text{O}_3, \text{SiO}_2), \text{Al}_2\text{O}_3, \text{SiF}_6]$ .

(666) ALUMINIC SULPHATE, or *Sesquisulphate of aluminum* ( $\text{Al}_2\text{SO}_4, 18\text{H}_2\text{O} = 343 + 324$ ), *Sp. Gr.* 1.671.—This salt is formed by dissolving alumina in sulphuric acid. It is now manufactured on a large scale in the north of England, by mixing finely-powdered clay or shale, after it has been gently roasted, with about half its weight of crude sulphuric acid from the chambers, heating it gradually until fumes of acid begin to escape; this digestion is continued for 3 or 4 days, after which the mass is lixiviated, and the solution thus obtained is freed from iron by the addition of sodic ferrocyanide so long as it occasions a blue precipitate; the clear liquid is decanted and evaporated, and the residue is sold under the name of *concentrated alum*. It crystallizes in thin flexible scales which are soluble in twice their weight of cold water: this solution may be used as a test for potassium, for by mixing it with a solution containing a salt of this metal, and evaporating, octohedral crystals of alum are deposited. Aluminic sulphate has a strong tendency to form double salts with monobasic sulphates, of which those with the sulphates of potassium and ammonium, constituting potash- and ammonia-alum respectively, are the most important. A remarkable anhydrous aluminic sulphate, which assumes the form of a white mealy powder, insoluble in cold water, but which may be rendered soluble, and converted into the ordinary sulphate, by prolonged boiling, is obtained by boiling either cryolite, or ordinary alum, with from three to ten times its weight of oil of vitriol, and distilling off about three-fourths of the sulphuric acid; the acid sulphate of potassium or of sodium, may be removed by washing, and the anhydrous aluminic sulphate is left as a white powder, analogous to the corresponding modification of the ferric and chromic sulphates (Persoz).

A basic aluminic sulphate, soluble in water, and of a yellow colour, may be obtained; the yellow tint is not due to the presence of ferric sulphate (Siewert).

(667) ALUM; *Potassio-aluminic sulphate* ( $\text{KAl}_2\text{SO}_4, 12\text{H}_2\text{O}$ ,  $= 258.5 + 216$ ); *Sp. Gr. anhydr.* 2.228; *cryst.* 1.726.—This valuable salt is occasionally found native in volcanic districts, in the form of a white efflorescence, produced by the action of the sulphuric acid of the volcano upon the compounds of aluminum and potassium contained in the lava and trachytic rocks. For

the purposes of commerce, however, alum is manufactured artificially. Three principal methods are adopted:—

1.—In the first the alum is procured by the addition of potassic sulphate or chloride to the crude aluminic sulphate prepared from clay by the process just described.

2.—A still simpler method is practised in Italy, where, especially in the neighbourhood of Civita Vecchia, the *alum-stone* is abundant. This rock contains the elements of alum, with an excess of hydrated alumina, mixed with a variable proportion of siliceous matter. The ore is first roasted at a gentle heat in kilns, avoiding direct contact with the fuel: water is thus expelled, and the mass is rendered spongy; the hydrated alumina parts with its water, and the formation of a basic sulphate of aluminum and potassium, which is insoluble in water, is thereby prevented: the roasted ore is then arranged in long heaps or ridges upon a firm clay floor, where it is frequently moistened with water: in the course of two or three months the mass crumbles down into a sort of mud, which is lixiviated: and the solution when evaporated yields crystals of alum, which after a second crystallization are fit for the market. This variety of alum, known as *Roman alum*, crystallizes in opaque cubes, which retain a variable amount of aluminic sulphate.

3.—A third process is resorted to in England and Germany for the purpose of turning alum schist, or *alum ore* as it is termed, to good account. This mineral is abundant at Whitby, in Yorkshire, and in the neighbourhood of Glasgow: it is a bituminous shale, found amongst the lower beds of the coal-measures, and it contains a large quantity of very finely divided iron pyrites, disseminated through its mass, which is composed chiefly of a siliceous clay. The mineral is decomposed either by exposure to the air, or, as is more usually practised, by a slow roasting, conducted upon the ore arranged with alternate layers of fuel in long heaps or ridges, which are covered more or less completely with spent ore, in order to regulate the heat and to absorb the excess of sulphuric acid. In this operation the pyrites, or ferric disulphide, is converted into ferrous sulphide, losing half its sulphur, which absorbs oxygen and is converted into sulphuric anhydride; this at the moment of its formation unites with the alumina, while the ferrous sulphide, gradually combining with more oxygen, is converted into ferrous sulphate, or green vitriol:  $2\text{FeS}_2 + 3\text{O}_2 = 2\text{FeS} + 2\text{SO}_2$ ; and  $\text{FeS} + 2\text{O}_2 = \text{FeSO}_4$ . Great care is required to prevent the temperature from rising too high, a circumstance which would be attended with decomposition of the aluminic sulphate and loss of sulphuric acid. By the time that the roasting is complete, the mass has become greatly reduced in bulk, and is rendered porous and freely permeable to the air; in this condition the heap is allowed to lie exposed to the atmosphere, and is moistened from time to time; it is then lixiviated, the

liquor is digested on metallic iron to reduce any ferric salt to the state of ferrous sulphate, and the green ferrous sulphate is separated from the aluminic sulphate by crystallization of the liquor. The mother-liquors often yield magnesian sulphate when concentrated further.

In the Whitby alum works, in which the quantity of the aluminic sulphate much exceeds that of the ferrous sulphate in solution, the concentration is completed in leaden pans; being carried so far as that the liquid shall, when cold, be perfectly saturated, but shall deposit no crystals. The liquid is then run off into the precipitating tank, where it is mixed with a saturated solution of potassic sulphate, or, what is better, of potassic chloride, in quantity sufficient (as found by trial on the small scale) to yield the maximum proportion of alum. The mixture is briskly agitated, and the potassio-aluminic sulphate, which is sparingly soluble in cold water, is deposited in minute crystals, technically termed *alum meal* or flour. When potassic chloride is used the ferrous sulphate is decomposed, potassic sulphate is produced, and the very soluble ferrous chloride is retained in the liquor;  $2\text{KCl} + \text{FeSO}_4 = \text{FeCl}_2 + \text{K}_2\text{SO}_4$ . To produce 100 parts of crystallized alum, between 18 and 19 parts of potassic sulphate are required, or about 16 parts of potassic chloride. The mother-liquor is drained off and preserved, and the crystals, which have a reddish-brown colour from adhering iron, are twice washed by subsidence with a small quantity of cold water, being well drained after each washing. The crystals are then dissolved by heat in as small a quantity of water as possible, and the solution is run off into crystallizing barrels, which in ten days or a fortnight are taken to pieces; the crystalline mass is broken into fragments, drained, and sent into the market.

In the Scotch alum works at Campsie, in the neighbourhood of Glasgow, alum meal is not formed; but the hot liquor from the evaporating pan is run into a stone cooler, in which the necessary quantity of dry potassic chloride has been placed. The liquid is thoroughly agitated and left to cool; on the sides of the vessel large crystals of alum are formed in four or five days. The mother-liquor is then drained off, and the crystals are afterwards washed and recrystallized twice.

Where ammoniac sulphate can be obtained sufficiently cheap, it is substituted for potassic sulphate in the manufacture of alum, as the double salt which it forms with aluminic sulphate crystallizes with almost as much facility as the potassium salt; it constitutes what is known as *ammonia alum*. In England at present

the greater part of the alum which is made is ammonia alum. Indeed, for the purposes to which alum is applied, neither the potassic nor the ammoniac sulphate is essential; the object proposed in the manufacture of alum being to obtain a salt of aluminum which, by the facility with which it crystallizes, can be freed from iron and from earthy impurities.

A number of other salts may be procured which have the same crystalline form as potassium alum, and are similar to it in constitution: for example, potassic sulphate may be displaced by sodic sulphate, and a sodium alum may be formed, but the compound is much more soluble than potassium alum: in like manner the place of the aluminic sulphate may be supplied by ferric, chromic, or manganic sesquisulphate, forming a remarkable series of isomorphous compounds, some of which are enumerated in the annexed table:—

Potassium alum	. $\text{KAl}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$	.
Sodium alum	. $\text{NaAl}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$	
Ammonium alum,	$\text{H}_4\text{NAl}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$	
Iron alum	. $\text{KFe}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$	
Chrome alum	. $\text{KCr}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$	
Manganese alum	. $\text{KMn}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$	

Besides these true alums, a number of aluminic double salts may be formed with the sulphates isomorphous with that of magnesium; they crystallize in fine silky needles. A native sulphate of aluminum and manganese was stated by Kane and by Apjohn to contain 25 atoms of water. A similar salt of iron has been met with in the native state. These fibrous salts, according to How, contain only  $22\text{H}_2\text{O}$ , so that the formula of the manganese salt would be  $\text{MnAl}_4\text{SO}_4 \cdot 22\text{H}_2\text{O}$ .

Ordinary alum has a sweetish, astringent taste; it is soluble in about 18 parts of cold water, and in less than its own weight of boiling water. The solution has a strongly acid reaction, and dissolves iron and zinc with evolution of hydrogen. When heated, this salt first melts in its water of crystallization, which amounts to 45.53 per cent. of its weight; as it loses water it froths up, and forms a tough, tenacious paste, which is ultimately converted into a voluminous, white, infusible, porous mass of anhydrous or *burnt alum*. If crystallized alum be submitted to a regularly increasing heat, a certain proportion of the water contained in it is readily driven off: thus by a temperature of  $212^\circ$ , 5 atoms out of the 12 are expelled, and 5 more at  $248^\circ$  ( $120^\circ \text{C.}$ ). If the salt be now heated to  $392^\circ$  ( $200^\circ \text{C.}$ ), it is rendered anhydrous and insoluble in water (Gerhardt). By ignition, alum loses a great part of its acid.

Alum is largely employed in dyeing: when used in this process its solution is gradually mixed with sodic carbonate, so long



as the precipitate is redissolved on agitation, which happens till two-thirds of the acid have been neutralized. The solution thus formed contains therefore a mixture of 3 salts, viz.,  $\text{Al}_2\text{O}_3\text{SO}_3 + \text{K}_2\text{SO}_4 + 2\text{Na}_2\text{SO}_4$ . Cloths dipped into this liquid remove the redissolved alumina, and contract an intimate mechanical combination with it, by which they are enabled, as already mentioned, to retain the colours of the dye-stuffs employed. Upon evaporation, cubic crystals of alum are deposited from this solution, and the excess of alumina separates. A basic hydrated aluminic sulphate ( $\text{Al}_2\text{O}_3\text{SO}_3 \cdot 9\text{H}_2\text{O}$ ), containing the same proportion of sulphuric anhydride and alumina as that formed in the mordanting liquid just described, is obtained by precipitating aluminic sesquisulphate incompletely by caustic ammonia; it is a white insoluble powder. A white earthy-looking mineral termed *aluminite*, said to have the same composition as this basic sulphate, is found near Newhaven.

(668) ALUMINIC PHOSPHATES.—Several minerals occur, into the composition of which aluminic phosphate enters. The blue *turquoise* is a hydrated native phosphate,  $\text{Al}_2\text{P}_2\text{O}_{11} \cdot 5\text{H}_2\text{O}$ , or  $2\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , coloured by copper and iron. *Gibbsite* which was formerly considered to be an aluminic hydrate, was found by Hermann to consist of a hydrated phosphate of the metal, mixed with a variable proportion of hydrated alumina. Aluminic phosphate ( $\text{AlPO}_4$ ) may be prepared artificially by mixing a solution of hydrodisodic phosphate with one of alum; the precipitate must be well washed. If this precipitate be redissolved in an acid, and ammonia be added, the precipitate thus occasioned has, according to Rammelsberg, the composition  $(4\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 18\text{H}_2\text{O})$ . *Wavellite* is a mineral which crystallizes in radiating tufts of needles; according to Berzelius, it is a combination of aluminic fluoride with the last-mentioned basic aluminic phosphate,  $3(4\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 18\text{H}_2\text{O}) \cdot \text{Al}_2\text{F}_6$ . The mineral *amblygonite* is a combination of fluoride and basic aluminic phosphate with trilithic phosphate. *Lazulite*,  $[2\{3[\text{CaMgFe}] \text{O} \cdot \text{P}_2\text{O}_5\} \cdot (4\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5) \cdot 6\text{H}_2\text{O}]$  is a blue mineral composed of another double phosphate which contains the same aluminic phosphate, coloured by basic phosphate of iron (Rammelsberg).

Aluminic phosphate, in its hydrated form, is readily soluble in hydrochloric acid. Its solution may be precipitated by caustic potash, but the precipitate is redissolved by an excess of the alkali. In the operations of analysis it is often necessary to separate phosphoric acid from alumina: this is most readily effected by Chancel's method, in which the solution in nitric or acetic acid, perfectly freed both from hydrochloric and sulphuric acid, is mixed with an acid solution of bismuth nitrate (448). Phosphoric acid is thus precipitated as bismuth phosphate ( $\text{Bi}'''\text{PO}_4$ ), and the whole of the aluminum remains in solution.

(669) ALUMINIC SILICATES.—The compounds of silica with aluminum are numerous and important. All the varieties of clay consist of hydrated aluminic silicate, more or less mixed with other matters derived from the rocks which, by their disintegration, have formed the clay. Clay is, in fact, the result of the combined action of air and water upon felspathic and siliceous rocks, and therefore necessarily varies considerably in composition. The fundamental constituent of the more important varieties of

clay, according to the researches of Brongniart, Malaguti, and others, is represented by the formula  $(\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O})$ . This appears to be the composition of the fire-clay of the Staffordshire coal-measures. The ordinary varieties of clay, however, contain fragments of undecomposed rock, a certain proportion of potash, and variable amounts of silica in the hydrated condition, mixed with lime, magnesia, and oxides of iron; the character of the clay is materially modified according as one or other of these ingredients predominates. The intermixture of lime, magnesia, or ferric oxide, in any considerable quantity, with the clay, greatly increases its fusibility, diminishes its plasticity, and causes it to be more readily attacked by acids: whilst an excess of silica renders it less fusible.

Pure clay, before it has been ignited, forms, when kneaded, a tenacious, plastic paste, which is insoluble in water, but may readily be diffused through it in particles which are in an extreme state of subdivision; the deposit, when freed from the excess of water, as it subsides, resumes its plastic character. This paste, when slowly dried, and exposed to a higher temperature, shrinks very much, and splits into masses which are extremely hard, but they do not undergo fusion in the furnace. Pure hydrated aluminic silicate is very slowly acted upon by hydrochloric or by nitric acid; but it is decomposed when heated with concentrated sulphuric acid; and upon this fact one of the processes for preparing alum (667) is founded. A gentle roasting of the clay, previous to the addition of the acid, frequently favours its disintegration; but ignition at a high temperature renders it proof against the action of acids, except the hydrofluoric. Strong solution of caustic potash dissolves unburnt clay very slowly; but if the hydrated alkali in excess be fused with clay, the resulting mass is easily soluble in water.

Clay emits the peculiar odour known as argillaceous when breathed upon or slightly moistened: its presence in any soil may be roughly but readily distinguished by the absorbent quality which it exhibits when applied in a dry state to the tongue or the lips; it adheres to them strongly, and absorbs the saliva from their surface. This absorbent property of clay causes it to retain ammonia in the soil to an extent which is of great importance to growing plants, and, as Way has shown, it arrests the ammoniacal portions of the manure applied to the surface, and thus not only ministers to the growth of the crop, but exerts a very important purifying influence upon water impregnated with organic and

other substances, which find their way slowly through the soil. Indeed, mere agitation of such water with finely divided clay is sufficient to remove a considerable amount of the organic and saline matter previously in solution. It was found that both sulphate and chloride of ammonium were partially decomposed by the lime of the clay, the ammonia being retained, whilst a corresponding amount of calcic sulphate or chloride was formed in the solution. A similar decomposing action was also exerted by clay upon potassic nitrate.

*Varieties of Clay.*—The most important varieties of clay are the following:—

1.—The celebrated *kaolin*, or porcelain clay of China, is a very pure white clay, furnished by the decomposition of a granitic rock, the constituents of which are quartz, felspar, and mica, the felspar having gradually mouldered into this substance. A very similar description of clay is obtained near St. Austel, in Cornwall, and at St. Yrieix, near Limoges, in France. It is in these cases chiefly produced by the disintegration of a rock known to geologists as *pegmatite*, which is, in fact, a species of granite in which mica is almost wanting, and quartz present in but small quantity. The *Cornish stone* used by the porcelain-makers is the same rock in a less advanced state of disintegration. The plasticity of kaolin is much less than that of the clay derived from disintegration of the secondary rocks.

2.—*Pipeclay* is a white variety of clay, which is nearly free from iron. That of the Isle of Purbeck, in Dorsetshire, where it occurs nearly at the base of the clay deposits, is preferred: it is used in the manufacture of tobacco-pipes without any addition; before the oxyhydrogen blowpipe it melts to a transparent, nearly colourless glass.

3.—The *blue clay* of Devonshire and Dorsetshire is highly prized, as it is eminently plastic. The organic matter to which it owes its colour is destroyed when heated, and it yields a white paste when fired. It is employed as one of the materials in the manufacture of porcelain. The upper beds of this clay frequently contain a large proportion of sand mixed with the plastic material, and are well suited for making salt-glazed stoneware without further admixture.

4.—When the proportion of calcic carbonate in a clay is considerable, it constitutes what is known as a *marl*; if the aluminous constituent preponderate, it forms an aluminous marl; if calcic carbonate be in excess, it is a calcareous marl. The

aluminous marls are extensively used in the manufacture of the coarser and more porous kinds of pottery.

5.—*Loam* is a still more mixed substance, belonging to the more recent alluvial formations: it is the common material of which bricks are made; its red or brown colour is derived from the large proportion of ferric oxide which it contains.

6.—*Yellow ochre* and *red bole* are clays which derive their colour from ferric oxide, which is present in them in large quantity.

*Halloysite* is a white hydrated aluminic silicate which greatly resembles kaolin in appearance, but it is destitute of any plastic character, and is therefore unfitted for the manufacture of porcelain. *Fuller's earth* is a porous aluminic silicate which has a strong adhesion to oily matters: if made into a paste with water, and allowed to dry upon a spot of grease upon a board or cloth, it removes most of the oil by capillary action. Amongst other localities in England, it is found abundantly near Reigate, in Surrey.

The following table exhibits the composition of some of the more important varieties of clay used in the arts. The first two are results obtained by Ebelmen and Salvétat; the others are from analyses executed in Richardson's laboratory, and are quoted in the second volume of the English translation of Knapp's *Technological Chemistry*:—

	Washed kaolin.			Stour- bridge fire-clay.	Pipe-clay.	Sandy clay.	Blue-clay.	Brick clay.
	Chinese.	St. Yrieix.	Cornish.					
Silica ...	50.5	48.37	46.32	64.10	53.66	66.68	46.38	49.44
Alumina ...	33.7	34.95	39.74	23.15	32.00	26.08	38.04	34.26
Oxide of iron	1.8	1.26	0.27	1.85	1.35	1.26	1.04	7.74
Lime ...	...	...	0.36	...	0.40	0.84	1.20	1.48
Magnesia ...	0.8	trace	0.44	0.95	trace	trace	trace	5.14
Potash and soda ... }	1.9	2.40	12.67	10.00	12.08	5.14	13.57	1.94
Water ...	11.2	12.62						
	99.9	99.60	99.80	100.05	99.49	100.00	100.23	100.00

Besides these amorphous aluminic silicates, there are many which occur in a crystalline form. *Disthene*, or *cyanite*, is a blue-coloured soft mineral of this kind ( $\text{Al}_2\text{O}_3, \text{SiO}_2$ ).

(670) *Other aluminous minerals*.—The *zeolites* are hydrated double silicates in which the principal bases are alumina and lime. They boil up when heated upon charcoal before the blow-pipe, (hence their name, from *ζέω*, to boil), and are dissolved by acids, leaving the silica in a gelatinous state. In these minerals the lime is liable to displacement more or less complete by ferrous oxide, by magnesia, or by the alkalis. They are often very beautifully crystallized. *Analcime* ( $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, 2\text{H}_2\text{O}$ ) is one of these minerals; it crystallizes in cubes. *Stilbite* crystallizes in radiated needles, and has the composition of hydrated labradorite ( $\text{CaO}, \text{Al}_2\text{O}_3, 6\text{SiO}_2, 6\text{H}_2\text{O}$ ). *Prehnite* crystallizes in

six-sided prisms; it may be represented by the formula,  $2\text{CaO}, \text{Al}_2\text{O}_3, 3\text{SiO}_2, \text{H}_2\text{O}$ .

The varieties of *felspar* ( $\text{M}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$ ) are likewise double silicates of aluminum with potassium, sodium, lithium, or calcium. Potassium-felspar, the *adularia* or *orthoclase* of mineralogists, and the *petuntze* of the Chinese potters, is sufficiently hard to scratch glass; it is used as a glaze in the manufacture of the finest kinds of porcelain. Felspar requires the most intense heat of the porcelain furnace for its fusion, when it forms a white milky glass. Sodium-felspar, from its usual white colour, has received the name of *albite*. The felspar containing lithium constitutes *petalite*. Common, or potassium-felspar, crystallizes in oblique rhombic prisms. *Labradorite* is a double aluminic silicate, analogous to felspar, but it contains calcium instead of the alkali-metals: it crystallizes in doubly oblique prisms belonging to the sixth system.

These minerals, by disintegration, yield the porcelain clay, or kaolin.

Felspar not only forms the regularly crystallized minerals just mentioned, but it occurs mingled with quartz and other crystallized minerals: it is indeed one of the most abundant constituents of many of the older rocks. *Granite*, for example, is a rock consisting of intermixed crystals of quartz, felspar, and mica. When it contains hornblende instead of mica, the term *syenite* is given to it. *Gneiss* contains the same components as granite, but it has a more stratified appearance, as the mica occurs more in layers. *Porphyry* consists chiefly of compact felspar, with crystals of felspar disseminated through it; it is often red or green, and takes a fine polish. *Basalt* is a dark-coloured volcanic rock, consisting of compact felspar containing crystals of augite. When the place of the feldspathic constituent is supplied by labradorite (or calcium felspar) the basalt is called *dolerite*. *Trap*, or *green-stone*, is a very tough, compact, igneous rock, of a dark-greenish or brownish-black colour; it is composed of an intimate mixture of felspar and hornblende. If it contain sodium-felspar (albite), the rock is known under the name of *diorite*. *Trachyte* is a volcanic rock also consisting chiefly of felspar, less compact than either porphyry or basalt. The porous *pumice-stone* of volcanic districts is probably altered felspar; it contains a much smaller proportion of alkali than the crystallized mineral. Melted pumice constitutes *obsidian*, or volcanic glass.

*Garnet*, which commonly crystallizes in rhombic dodecahedra,

and *idocrase*, which crystallizes in square prisms, are basic double silicates of calcium and aluminum, in which part of the lime is displaced by other protoxides, and the alumina by sesquioxide of iron  $[3(\text{CaMgFeMn})'''\text{O}, (\text{AlFe})'''\text{O}_3, 3\text{SiO}_2]$ . In *pyrope*, which is a species of garnet found in Bohemia, the colouring matter is partly chromic oxide. These minerals have a hardness greater than that of quartz.

The different forms of *mica* are also double aluminic silicates, which contain in addition a small quantity of water and some alkaline fluoride. *Uniaxal* mica consists chiefly of magnesian and aluminic silicate  $[4(\text{MgKFe})\text{O}, (\text{AlFe})_2\text{O}_3, 4\text{SiO}_2]$ . In *biaxal* mica  $[(\text{KFe})\text{O}, 3(\text{AlFe})_2\text{O}_3, 6\text{SiO}_2]$ , on the other hand, potassic silicate predominates. *Lepidolite* is a variety of biaxal mica in which lithic silicate takes the place of potassic silicate.

Another important alumino-magnesian silicate constitutes *chlorite*  $[4(\text{MgFe})\text{O}, (\text{AlFe})_2\text{O}_3, 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}]$ , which occurs both massive and in crystals with a granular fracture; it is of a green colour. In the massive form of chlorite slate it occurs as one of the primitive rocks which is widely distributed. There are many varieties of slate. *Roofing slate* is an argillaceous rock which splits readily into thin laminæ. *Mica slate*, as its name implies, contains particles of mica, to which it owes its glistening appearance. *Hornblende slate* contains hornblende in place of mica, and has little lustre.

(671) *Porcelain and Pottery Ware*.—In the preparation of earthenware the material employed is required to possess a plasticity equal to that of red-hot glass, and yet to be capable of being rendered by heat sufficiently firm and hard to resist the mechanical violence necessarily inflicted on it by daily use.

The basis of earthenware, porcelain, and china, is aluminic silicate: it possesses the plasticity required, and when heated assumes a great degree of hardness. Pure aluminic silicate, however, contracts greatly and unequally on drying: the utensils made from it would consequently be liable to crack during their desiccation; in order, therefore, to diminish the amount of this contraction, an addition of some indifferent powder, such as ground flint, is made; while to compensate for the loss of tenacity thus occasioned, and which is particularly experienced in the use of the fine clays employed for porcelain, some fusible material is added, which, at the temperature required for firing, undergoes vitrification, and greatly assists in binding the mass

together. According to the greater or less proportion of these fusible materials, the ware is more or less semi-transparent, and more or less subject, like glass, to fly on the application of sudden changes of temperature.

The articles which have passed once through the kiln, and have thus acquired firmness, are rough and uneven, and the coarser kinds of ware are very porous. It is usual, after the first firing, in order to give smoothness and uniformity to the surface, as well as to render the body of the ware impermeable to moisture, to cover it with a kind of flux or glaze, which melts at a lower temperature than the material composing the ware itself; and in order to melt the glaze the articles are a second time passed through the kiln.

The materials employed in the fabrication of porcelain and earthenware are, clays of various degrees of purity and fineness, ground felspar, calcined flints or sand, burnt bones, chalk, and sodic or potassic carbonate; they do not, therefore, differ very greatly from those which are employed in glass-making except in the great preponderance of aluminic silicate. The varieties of pottery or earthenware are numerous: the following include those which are of most importance:—

1.—*Porcelain, or China.*—This is the finest and most valuable description of ware: it is distinguished from ordinary earthenware by the composition of the paste from which it is formed. The materials are selected with great care, in order that they may give a colourless mass after firing. Porcelain consists mainly of two classes of materials, one of which, the clay, is plastic, and is infusible at the temperature employed to fire it; the other (chiefly calcic and potassic silicate) softens and becomes vitrified, forming a kind of cement which binds the clay firmly together, and thus produces a translucent mass, which, when broken appears to be of a uniform texture throughout, and is impervious to liquids. Much judgment is required in the due proportioning of the fusible and infusible materials.

The celebrated Sèvres porcelain resembles the original Chinese ware, of which indeed it is an imitation. Regnault states the composition of the paste used at Sèvres for ornamental purposes to be the following:—Washed kaolin, 62 parts; Bougival chalk, 4; Aumont sand, 17; quartzose felspar, 17. These ingredients are carefully levigated and then thoroughly incorporated. As, however, the composition of the kaolin varies, the proportion of the other materials is necessarily varied likewise, so as to obtain a porcelain of uniform composition.

In order to give a smooth surface to the ware, a glaze similar in composition to the fusible material is used. The glaze employed at Sèvres consists of a mix-

ture of felspar and quartz. It is transparent, and rather more fusible than the body of the ware, but becomes thoroughly incorporated with it, and from its similarity in composition it expands and contracts by heat uniformly with the paste which it covers; hence it is not liable to crack and split in all directions in the manner which is so commonly observed in the glaze of the more ordinary kinds of earthenware.

The china of Berlin and Meissen is very similar in composition to that of Sèvres: these constitute what is termed hard, or true, porcelain.

English porcelain contains, in addition to the Cornish clay and felspar or flint, a large proportion of burnt bones; the glaze, which is transparent, usually contains both borax and plumbic oxide to increase its fusibility. English porcelain is softer than the Chinese, French, or German porcelain, and constitutes one variety of what the French term *porcelaine tendre*, the manufacture of which in France is now rarely practised.

2.—*Stoneware* is a species of porcelain in which the body of the ware is more or less coloured, less care being taken with regard to the purity of the material. It generally contains more oxide of iron, and consequently is somewhat more fusible than the best porcelain, and is usually salt-glazed in a manner shortly to be described. *Wedgwood-ware* is a fine description of stoneware.

3.—*Fine Earthenware*.—Articles of this description are very extensively manufactured in the Staffordshire Potteries, and constitute the ordinary table-service of this country. The Devonshire and Dorsetshire clays are those chiefly made use of; they are mixed with a large proportion of ground flints, and yield an infusible paste which burns nearly white. The body of the ware is not fused in the firing, but it is rendered impervious to liquids by means of a fusible lead glaze.

4.—*Common earthenware* is made of an inferior and more fusible description of clay: both this kind of ware and the foregoing one crack easily on the sudden application of heat.

5.—The coarsest description of clay goods are bricks, tiles, flowerpots, and similar articles.

6.—Articles which are required to stand a high temperature, such as fire-bricks for lining furnaces, muffles, pots for the fusion of glass, crucibles for melting steel, and the Hessian crucibles so largely in demand in the laboratory, are made of a pure, infusible siliceous clay, the shrinking of which during drying is diminished by the addition either of burnt clay of the same description, or of, what amounts to the same thing, broken pots of the same material, which are reduced to a fine powder and incorporated with the paste. Good fire-ware is nearly white: if coloured, the presence of oxide of iron would be indicated, and this would render it fusible.



The following table gives the composition of some of the more important varieties of china and pottery ware:—

	Porcelain.					Wedg-wood ware.	Lambeth stone-ware.	Hessian crucible.
	Chinese.	Berlin.	English.	Sèvres.	Meissen.			
	O.Cowper	Wilson.	Cowper.	Laurent.	Laurent.	Salvetat.	Salvetat.	Berthier.
Silica ...	71·04	71·34	40·60	58·0	57·7	66·49	74·00	71
Alumina ...	...	23·76	24·15	34·5	36·0	26·00	22·04	25
Oxide of iron ...	22·46	1·74	...	...	0·8	6·12	2·00	4
Lime ...	3·82	0·57	14·22	4·5	0·3	1·04	0·60	
Alkali ...	2·68	2·00	5·28	3·0	5·2	0·20	1·06	
Magnesia ...	...	0·20	0·43	...	trace.	0·15	0·17	
Bone earth and oxide of iron ...	...	...	15·32					
	100·00	99·61	100·00	100·0	100·0	100·00	99·87	100·0

(672) *Manufacture of Porcelain.*—For the finer kinds of porcelain much care is taken to ensure the purity and minute subdivision of the constituents, as well as their intimate admixture. The clay is first ground between horizontal stones under water; it is next levigated in water, to allow the coarser particles to subside while the lighter ones remain in suspension. The finer suspended particles are then formed into a mixture of the consistence of thin cream, a wine pint of this being made to weigh 24 or 26 ounces: in this state the cream or pulp is mixed with the ground felspar, flint, or other material. Suppose, for example, that the pulp is to be mixed with ground flints; the flints are heated to redness, suddenly quenched in cold water, and then reduced by stamping and grinding them under water to an impalpable powder; this also is suspended in water, a wine pint of the mixture being made to weigh 32 ounces. The two ingredients are easily mixed in the necessary proportions by taking a given measure of each pulp and thoroughly incorporating them. The mixture thus obtained is technically termed *slip*. The slip is well agitated and allowed to subside; the deposit is drained (carefully mixing it from time to time), and dried, until it has acquired sufficient consistence to allow of its being wrought by the potter. Much labour is afterwards bestowed in working this clay in such a manner as to render it of uniform composition throughout, and to preserve it free from air-bubbles. The mixture is found to be greatly improved in quality by being allowed to remain for some months before it is worked up, the mass being occasionally turned over and beaten. During this process of ripening the mass undergoes a slow change, in the course of which traces of organic matter which it contains gradually become oxidized, reducing the sulphates to sulphides, in consequence of which it evolves a slight odour of sulphuretted hydrogen, and the colour of the paste becomes somewhat darker from the formation of traces of ferrous sulphide. It is of great importance in the finer specimens of ware to avoid the presence of organic matter: a single hair might spoil a delicate work of art by the disengagement of gas, and the formation of bubbles in the interior of the mass when heated.

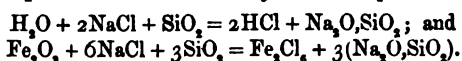
Less labour is expended upon the coarser kinds of pottery. After the raw clay, brought from Devonshire or Dorsetshire in blocks of about 30 pounds weight (or nearly 14 kilos.), has been dried, it is ground and mixed with a certain proportion of ground flints; it is then tempered with water into a stiff paste, and passed between rollers to complete the process of fitting it for the wheel.

The mechanical operations are of the same nature in every case: and, for fashioning the clay, the *potter's wheel* is in general use. This consists of a circular slab, which can be made to revolve in a horizontal plane, either by a treddle or by a winch turned by a boy or girl. A mass of clay of the size required is dashed upon the moistened slab, and is worked by the hands, the wheel revolving during the whole time, so that the operation is a compound of moulding and turning; the article is finally trimmed up with a wooden tool, and the work is detached from the wheel by passing a wire between the slab and the vessel. The moulded articles are then allowed to dry for a day or two in a room heated from  $90^{\circ}$  to  $100^{\circ}$  ( $32^{\circ}2$  to  $37^{\circ}8$  C.), in order to give firmness sufficient to permit them, when necessary, to be carefully turned on a lathe. After this operation has been completed, the handles and ornaments may be attached; these are made in moulds, and adhere readily by means of slip when pressed against the moulded mass, which is still moist. The articles have at this stage received the form which they are intended to retain, and are next subjected to heat in the *biscuit* furnace. It is necessary that the temperature be at first very gradually and carefully raised, lest the aqueous vapour, being extricated too suddenly, should deface the vessel or injure its texture. By this first firing the different articles acquire a greater degree of firmness, and can be handled without danger of breakage, but they are in a very porous state, technically termed *biscuit*. The ware in this stage readily absorbs any solution that may be placed upon its surface, and this is the period chosen for printing the patterns or designs which the finished goods are to exhibit. The colouring matter generally consists of some metallic oxide ground up with oil of turpentine or with boiled linseed oil. Blue is usually given by cobalt oxide; green by chromic oxide; brown by a mixture of oxides of iron and manganese; black, by black uranium oxide; and a pink, which is much esteemed, by a combination of stannic oxide, lime, and a minute quantity of chromic oxide. In order to apply the colouring material, it is printed from copper plates on a thin unsized paper made for the purpose; this paper, while the colour is still moist, is applied to the surface of the biscuit; the design is soon absorbed by the ware, and the paper is washed off. The ware is now subjected to another baking or firing, for the purpose of fixing the colour and burning off the oil. For decorating the finer kinds of porcelain the metallic colour is mixed with a fusible glaze containing quartz, boracic acid, and plumbic oxide melted together. The coloured glass thus obtained is then reduced by levigation to a fine powder, and ground up with some volatile oil, in which form it is laid on in the desired pattern by means of a hair pencil. After the glazing has been completed, it is fired at a moderate heat in a muffle. In the finer kinds of decoration, the application of the colouring matter requires the nicest management. For details upon this point (and indeed upon most others connected with the art of Pottery), the reader is referred to Brongniart's great work *Sur les Arts Ceramiques*. After the application of the colouring material, the ware still remains far too porous for use, and it further undergoes the process of glazing.

The glaze for fine porcelain is prepared by levigating quartz and felspar with water, so as to form a mixture of the consistence of cream; to this a little vinegar is added, to favour the suspension of the finely divided particles. Each article is then dipped separately into the mixture. The porous mass quickly absorbs the moisture, leaving a thin uniform film of glaze upon the surface. The goods thus prepared are then enclosed in vessels made of fire-clay, termed *seggars*, and are exposed to the most intense heat attainable in the porcelain furnace.

In glazing ordinary earthenware a similar process is adopted, but the temperature of firing is below that required in the biscuit furnace. The glaze usually consists of a fusible material containing a considerable quantity of plumbic oxide; a mixture of felspar, flint, flint glass, and white lead, is in common use.

The glazing of stone-ware depends upon a peculiar mode of decomposition of common salt. Sodium chloride is not decomposed by heat alone, and if heated with dry silica no decomposition occurs; but in the presence of silica and some substance capable of imparting oxygen to the sodium, and at the same time of removing the chlorine with which it is united—such, for instance as steam, or ferric oxide—the salt is susceptible of decomposition at an elevated temperature; sodic silicate and hydrochloric acid, or sodic silicate and ferric chloride, as the case may be, being formed. The various utensils, having been dipped into sand and water, are placed in the kiln, and are gradually raised to an intense heat. A certain quantity of moist salt is then thrown in: the sodic chloride is quickly converted into vapour, and the salt is decomposed by the silica and ferric oxide in the clay, aided by the steam produced in the combustion of the fuel in the furnace. The ferric chloride and hydrochloric acid pass off in vapour with the excess of salt employed, whilst the sodic silicate fuses upon the ware, and renders it impervious to liquids. The reactions may be thus represented:—



It is worthy of remark, that although clay contracts very evenly by heat when its density is uniform throughout, yet if its density be unequal in different parts, the contraction is also unequal; hence though a vessel may issue smooth and well finished from the workman's hands, it often assumes a striated and uneven appearance during the process of firing; and if a stamp be impressed upon clay while soft, and the whole surface be shaved away until no further impression is visible, the mark of the stamp, after baking, reappears in a manner more or less distinct.

(673) *Ultramarine*.—Alumina enters into the formation of the pigment ultramarine, so highly prized for the purity and delicacy of its blue colour, and for its permanence when exposed to light and air, though mixed with oils, and subjected to the action of lime or of alkalis. This valuable colouring material was formerly obtained exclusively from the lapis lazuli by a tedious process, which consisted in gently calcining the stone, broken into fragments of the size of hazel-nuts; the heated fragments were then quenched in vinegar, by which they were rendered more friable, and were deprived of adhering calcic carbonate: they were next subjected to a patient levigation with a thin syrup of honey and dragon's-blood; were then made into a paste with a resinous cement; and after allowing this to remain undisturbed for some days, the ultramarine was extracted from it by suspension in hot water and subsidence.

Ultramarine is now, however, manufactured artificially upon a large scale; and, amongst other applications, it is extensively used in paper-staining. The following process answers well upon the small scale:—100 parts of finely washed kaolin, 100 of sodic carbonate, 60 of sulphur, and 12 of charcoal, are intimately mixed, and exposed in a covered crucible to a bright red heat for three hours and a half. The residue, which should not be in a fused condition, is of a green colour. It must be well washed, dried, and mixed with a fifth of its weight of sulphur, and exposed in a thin layer to a gentle heat, little above that required to burn off the sulphur. When the sulphur has all been burned off, a fresh

quantity of sulphur must be added, and the roasting repeated; and this roasting, with fresh additions of sulphur, must be repeated two or three times until the mass acquires a bright blue colour. Other proportions of the ingredients may be used, the temperature varying with the composition: the heat should be as high as the mass will bear, provided it is not fused. The green modification of ultramarine is also manufactured for the market; by oxidation the green may be converted into the blue form. Blue ultramarines vary in tint, some being pure blue, others greenish blue, and others violet blue, with a roseate reflex. The violet ultramarines are well adapted for use in paper-staining, as they withstand the action of the alum used in sizes, which the two other tints do not.

Considerable doubt still exists as to the true nature of the colouring matter of ultramarine, which has been made the subject of study by many chemists. According to the experiments of Wilkens,—who has made careful analyses of a variety of samples of the artificial product, both from his own manufactory and from other sources—ultramarine is composed of two portions, one of which is constant in composition; and which he regards as the essential colouring body; it is attacked with facility by hydrochloric acid, evolving sulphuretted hydrogen: the other portion is not soluble in the acid, and contains a variable amount of sand, clay, ferric oxide, and sulphuric acid. His analysis of the pure blue pigment corresponds nearly with the formula  $(2\text{Al}_2\text{O}_3, 3\text{SiO}_2 \cdot \text{Al}_2\text{O}_3, 4\text{SiO}_2 \cdot \text{Na}_2\text{S}_2\text{O}_8 \cdot 3\text{Na}_2\text{S})$ , which would contain, in 100 parts:—

By calculation.		By experiment.		
$\text{SiO}_2$	= 37·6	40·25	39·39	40·19
$\text{Al}_2\text{O}_3$	= 27·4	26·62	26·40	25·85
S	= 14·2	13·42	12·69	13·27
$\text{Na}_2\text{O}$	= 20·0	19·89	21·52	20·69

He states that the presence of iron is found not to be essential to the production of the colour: but this is still a matter of doubt. According to Brunner, a corresponding compound, in which dipotassic sulphide is substituted for disodic sulphide, is colourless.

Ultramarine, if heated in the air, gradually assumes a dull green hue; when heated with sulphur, it is not changed; if melted with borax, sulphur and sulphurous anhydride escape, and a colourless glass remains. Sulphuric, nitric, and hydrochloric acids decompose it, and the colour is quickly destroyed. Chlorine acts still more rapidly, dissolving everything but the silica, and completely discharging the colour.

(674) CHARACTERS OF THE COMPOUNDS OF ALUMINUM.—The ordinary salts of aluminum, with the exception of the chloride, are colourless. They have a sweetish, strongly astringent taste, and an acid reaction upon litmus.

*Before the blowpipe* the compounds of aluminum are distinguished by the formation of a pale azure blue if moistened with cobalt nitrate and gently ignited.

In solution they give with *ammonic hydrosulphide*, a white precipitate of hydrated alumina, with evolution of sulphuretted hydrogen. *Ammonia* produces a bulky, semi-transparent, gelatinous precipitate of hydrated alumina, which is nearly insoluble in excess of ammonia, or of its carbonate. *Caustic potash* dissolves it readily; and it is reprecipitated on adding solution of ammoniac chloride in excess. The *carbonates of the alkali-metals* produce the same precipitate under disengagement of carbonic anhydride, but, according to Muspratt, it retains a portion of carbonic acid. *Potassic sulphate* and sulphuric acid in slight excess added to solutions of the salts of aluminum, and evaporated, furnish well-marked octohedral crystals of alum.

*Estimation of Alumina.*—The quantity of alumina in the course of an analysis is always estimated from the precipitate by ammonia, or its carbonate or hydrosulphate; when thoroughly washed (an operation which, from its gelatinous nature, is tedious), and then ignited, it consists of the pure earth only.

(675) *Separation of Alumina from the Alkalies and Alkaline Earths.*—Supposing a magnesium salt to be present in the liquid, a solution of ammoniac chloride is first added to it, unless it be powerfully acid; on the addition of caustic ammonia in slight excess, pure hydrated alumina is precipitated. Ammonic hydrosulphide is a still better precipitant, if the liquid has been first nearly neutralized by ammonia; the precipitate is extremely voluminous, and requires persevering washing. On ignition it yields pure alumina. The alkalies and alkaline earths remain in the solution which has been filtered from the alumina, and their amount may be determined by methods hereafter to be detailed (694 *et seq.*).

§ II. GLUCINUM: ( $G'' = 9.5$ ). *Sp. Gr.* 2.1. *Atomic Vol. solid* 4.44.

(676) GLUCINUM, the *beryllium* of German writers, is extracted from the emerald, or the beryl, which consists chiefly of silicate of aluminum and glucinum ( $3\text{GO}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$ ). The metal is procured from its chloride in the same way as aluminum. *Phenakite* is a glucinic silicate ( $2\text{GO}, \text{SiO}_2$ ).

Glucinum, according to the experiments of Debray (*Ann. de Chimie*, III. xlv. 5), is a white, malleable metal, fusible below the melting-point of silver. It does not burn in air, oxygen, or the vapour of sulphur, but it combines readily with chlorine and iodine, and also with silicon. The vapour of water is not decomposed by it, even when the metal is heated to full redness and exposed to it. Glucinum is easily dissolved by diluted hydrochloric and sulphuric acids; nitric acid, whether diluted or concentrated, acts but feebly upon it. It is, however,

readily dissolved by a solution of potash, with evolution of hydrogen, but is not acted upon by ammonia. Glucinum forms but one oxide; there is some doubt whether this should be regarded as a protoxide, or as a sesquioxide. Berzelius adopted the latter view, but later researches favour the supposition that it is a protoxide.

(677) GLUCINA ( $GO = 25.5$ ; *Sp. Gr.* 2.967) is extracted from the beryl, of which it constitutes 13.6 per cent.: the mineral is reduced to a very fine powder, and fused with potassic carbonate;\* treated with hydrochloric acid, evaporated to dryness, again moistened with acid and treated with water; in this way everything except the silica is dissolved: the filtered liquid is mixed with an excess of a solution of ammonia, which occasions a voluminous precipitate containing both alumina and glucina; this precipitate is well washed, and the glucina is dissolved out from the alumina by digesting the mass in a solution of ammoniac carbonate. It is again filtered, and upon boiling the clear liquid, glucinic carbonate is deposited as a white powder, which, when ignited, leaves pure glucina. Freshly precipitated glucina forms with water a somewhat tenacious mass, but it does not harden like alumina when ignited. Ebelmen obtained it in crystals, by operating at a high temperature, as upon alumina (72); it formed minute six-sided prismatic crystals of the same form as those of zinc oxide. The fixed alkalis and their carbonates dissolve glucina readily; but the dilute solution in caustic potash deposits glucina when boiled. Hydrate of glucina yields a bulky, white, gelatinous mass, which absorbs carbonic acid from the air. When heated with solutions of the salts of ammonium it displaces ammonia, and is gradually dissolved. *Glucinic chloride* ( $GCl_3 = 80.5$ ) is prepared in the same way as aluminic chloride: it sublimes in white, brilliant, fusible needles, which are very deliquescent; a hydrated chloride with  $4H_2O$  may be obtained in crystals. Glucinum yields several sulphates; one of these ( $GSO_4 \cdot 4H_2O$ ) crystallizes in octohedra; the other sulphates are amorphous subsalts. It does not form an alum with potassic sulphate, but yields a double salt, in which the proportion of sulphur is divided equally between the two basyls ( $K_2G_2SO_4 \cdot 2H_2O$ ). A glucinic *aluminate* coloured with ferric oxide occurs native in the gem *chrysoberyl* ( $GO, Al_2O_3$ ). Glucinic carbonate forms double salts with the carbonates of potassium and ammonium.

(678) CHARACTERS OF THE GLUCINIC SALTS.—The salts of glucinum have a sweet taste (whence the name glucinum was derived, from  $\gamma\lambda\upsilon\kappa\upsilon\varsigma$ , sweet), with a slight astringency, and have an acid reaction upon litmus. They are colourless, and are distinguished from those of aluminum by not yielding an alum with potassic sulphate; nor a blue when heated before the blowpipe with cobalt nitrate; and by giving with *ammonic carbonate* a white precipitate of glucinic carbonate easily soluble in excess of the alkaline salt. *Potassic ferrocyanide* gives no precipitate in their solutions: a white precipitate of hydrated glucina is produced by *dipotassic sulphide*, with extrication of sulphuretted hydrogen. If a hot solution of *potassic fluoride* in excess be added to a hot solution of a glucinum salt, scales of a sparingly soluble double fluoride of glucinum and potassium are formed.

Glucinum is always estimated in the form of the anhydrous earth.

### § III. YTTRIUM, ERBIUM.

(679) YTTRIUM ( $Y = 61.7$ ) is obtained by a method similar to that employed for aluminum and glucinum. This metal is not oxidized when heated to redness

\* Debray finds it advantageous to substitute for the potassic carbonate quicklime, in proportion of half the weight of the beryl employed.

either in air or in aqueous vapour; in oxygen it burns with superb scintillations; solutions of the alkalies and the dilute acids dissolve it slowly.

*Yttria* (YO = 77·7) is a very rare earth, found in *gadolinite*, a mineral which occurs at Ytterby, in Sweden, and which is a silicate of yttrium, glucinum, cerium, and iron; it occurs also in *yttrotantalite* combined with tantalum, and in one or two other very rare minerals. It is considered to be a protoxide, and forms a white earthy powder of sp. gr. 4·842; it is insoluble in the caustic alkalies, but the carbonates of the alkali-metals dissolve it; ammoniac carbonate dissolves it still more freely.

The salts of yttrium are colourless; they have a sweetish astringent taste; their solutions yield a white precipitate with potassic ferrocyanide, and with the soluble oxalates. The most characteristic salt of yttrium is the sulphate, the crystals of which lose water at 176° (80° C.), and become milk-white, without change of form; on being put into water they do not resume their transparency.

(680) Mosander supposed that three bases had been confounded under the name of yttria: to the more abundant of these he gave the name of yttria; the other two he distinguished as *erbia* and *terbia*. The oxide of erbium (EO = 128·6?) is feebly rose-red, and its salts have a similar colour and a sweetish astringent taste. The solutions of these salts furnish when viewed by transmitted light a spectrum marked by highly characteristic absorption bands. The body supposed to be *terbia* has since been shown by Bahr and Bunsen to be a mixture of yttria and *erbia*. (*Liebig's Annal.* cxxxvii. 1.) *Erbia*, according to the same observers, when introduced into a Bunsen burner, glows with an intense green light, which when viewed through the spectroscope furnishes a continuous spectrum crossed by brilliant streaks, so that *erbia* is the only solid substance known which gives a spectrum, crossed by bright lines, not due to the volatilization of the substance. The solutions of its salts give absorption spectra, in which the dark lines correspond exactly with those of the spectrum of incandescence.

#### § IV. CERIUM, LANTHANUM, AND DIDYMIUM.

(681) THE three metals now to be mentioned need no lengthened description, as they have hitherto been found only in a few rare minerals, of which *cerite*, a hydrated basic ceric silicate, is the most common.

CERIUM (Ce = 92) appears to form two oxides—a protoxide, and a sesquioxide, both of which yield salts with acids. The best known of these are cerous oxalate and the cerous-potassic sulphate, which latter salt is insoluble in a solution of potassic sulphate. Cerous oxalate ( $\text{CeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ ) has been given in doses of from 0·13 to 0·26 grm., or from 2 to 4 grains, with good effect, in some cases of obstinate vomiting, and in some forms of pyrosis. The ceric sesquioxide has a yellowish tinge, and its salts are yellow or red.

(682) LANTHANUM (so named from *λανθάνω*, to lie hid) (La = 92) was discovered by Mosander, in 1841. It forms only one oxide, which is buff-coloured,

and freely soluble in diluted nitric acid. It forms colourless, astringent salts, which give a white precipitate with the soluble oxalates.

DIDYMIUM (so named from *δίδυμος*, twin, in reference to its close association with lanthanum) ( $\text{Di} = 96$ ) is scarcely known in the metallic form: it furnishes but a single oxide, which is of a dark-brown colour, when anhydrous: in the hydrated state it is insoluble in solutions of potash and ammonia: but it absorbs carbonic acid from the air. It furnishes a sparingly soluble white oxalate, and yields rose-white double sulphates with the sulphates of potassium, sodium, and ammonium. Its solutions, when viewed through a prism by transmitted light, show a strong absorption line in the yellow, and another in the green (Part I. p. 166). A detailed description of this spectrum is given by Bahr and Bunsen (*Liebig's Ann.* cxxxvii. 19). Didymium salts are pink or violet-coloured, and are not precipitated at ordinary temperatures by ammoniac hydrosulphide.

## CHAPTER XV.

### GROUP IV.—MAGNESIAN METALS.

#### MAGNESIUM—ZINC—CADMIUM.

Metal.	Sym- bol.	Atomic weight.	Atomic volume.	Specific heat.	Fusing point.		Boiling point.		Sp. gr.	Electric conductivity at 0° C.
					° C.	° F.	° C.	° F.		
Magnesium	Mg	24.3	13.76	0.2499					1.743	25.47*
Zinc ... ..	Zn	65	9.12	0.0955	412	773	1040	1904	7.146	29.02
Cadmium ...	Cd	112	12.96	0.0567	228	442	860	1580	8.604	23.72

THESE metals are all volatile, and burn in air with a powerful flame when strongly heated. They furnish but one basic oxide, and yield very soluble chlorides and sulphates; magnesian sulphide is to some extent soluble; zincic and cadmic sulphides are insoluble. These metals have a strong tendency to form basic carbonates; their corresponding salts are isomorphous.

§ I. MAGNESIUM: ( $\text{Mg}'' = 24.3$ ). *Sp. Gr.* 1.743.

(683) MAGNESIUM is usually classed with those metals the oxides of which furnish the alkaline earths, but it is much more analogous to zinc in its properties than to any other element. Magnesium is an abundant ingredient of the crust of the earth. It is found in combination in large quantities as a magnesio-calcic carbonate, forming magnesian limestone, or dolomite. It is contained abundantly in sea-water as chloride, and in many springs as sulphate. It likewise enters more or less extensively into the formation of many rocks, and of a great variety of minerals.

\* At 62° 6 (17° C.).



*Preparation.* 1.—Bussy obtained magnesium in the metallic form by heating its anhydrous chloride with potassium in a porcelain or platinum crucible. When cold, the contents of the vessel were digested in cold water, by which the potassic chloride and undecomposed magnesian chloride were dissolved out. The metal was left as a grey powder, which could be melted into globules.

2.—Deville and Caron (*Comptes Rendus*, xlv. 394) obtain the metal as follows:—600 grms. (or  $1\frac{1}{2}$  lb.) of pure magnesian chloride are mixed with 100 grms. of fused sodic chloride, and 100 of pure calcic fluoride, both in fine powder. 100 grms. of sodium in small fragments are carefully mingled with the powder—the whole is thrown into a clay crucible at a full red heat, and it is then instantly covered. When the mixture has become tranquil, the cover is removed, and the fused mass is stirred with an iron rod, in order to render it homogeneous throughout, and to obtain a clean surface upon the liquid. Globules of magnesium are then distinctly visible. The crucible is allowed to cool partially, and the metallic globules are united by means of the iron rod; the melted mass is then poured upon a shovel, and the magnesium, amounting to about 45 grms. ( $1\frac{1}{2}$  ounces), is separated from the slag. The magnesium may be placed in a porcelain tray and collected into one mass by melting it in a current of hydrogen; after which it may be purified by remelting in a bath of mixed magnesian chloride, sodic chloride, and calcic fluoride. It still, however, usually retains portions of carbon, silicon, and nitrogen, from which it may be purified by careful distillation in a current of hydrogen. Sonstadt prefers to decompose the magnesio-sodic chloride by means of sodium; and he then distils the metal in an iron crucible arranged as in the ordinary mode of distilling zinc; fig. 353. He prepares it by this method for commercial purposes on a considerable scale.

3.—Bunsen (*Liebig's Annal.* lxxxii. 137) procures magnesium by the electrolytic decomposition of magnesian chloride; this salt he melts in a deep covered porcelain crucible divided by a vertical diaphragm of porcelain, which extends half-way down the crucible; the electrodes are made of carbon, and are introduced through two openings in the lid, the negative electrode being notched to receive the reduced magnesium which lodges in the cavities: the crucible is brought to a red heat, and is filled with the melted chloride, which then is readily decomposed by 10 cells of the zinc carbon battery (266). The principal difficulty in this operation arises from the small density of the reduced metal, which rises to the surface of the fused salt, and is liable to reoxidation.

*Properties.*—Magnesium is a malleable, ductile metal of the colour of silver; it takes a high polish, and preserves it nearly as well as zinc at ordinary temperatures in dry air; but in a moist atmosphere it becomes slowly oxidized. Its fracture appears sometimes to be crystalline, at other times fibrous. It has about the same degree of hardness as calc-spar. At a moderate red

heat it may be melted. It may be converted into wire by heating the metal in the cylinder of a press until it softens, and then forcing it through holes in a die which forms the bottom of the press; the wire may be converted into a flattened ribbon by passing it between heated rollers. When ignited in dry air or in oxygen gas, magnesium takes fire and becomes oxidized; in the form of wire it burns easily, emitting a light of dazzling brilliancy, which has lately been employed as an artificial light for photographic purposes; the magnesia which is produced exhibits no sign of fusion. Deville and Caron have shown that magnesium is nearly as volatile as zinc, and that it may be distilled by heating it strongly in a current of hydrogen. A portion of the metal is carried away in suspension by the gas, and if the latter be kindled as it issues from the apparatus, it burns with a beautiful and highly luminous flame. Magnesium is but slowly acted upon by cold water, but it is rapidly dissolved if the water be slightly acidulated. It is also freely soluble in a solution of sal ammoniac. When thrown into strong hydrochloric acid it bursts into flame; yet a mixture of concentrated sulphuric and fuming nitric acid has no action upon it unless it be heated. When heated in chlorine and in the vapour of bromine, of iodine, or of sulphur, it burns brilliantly. Magnesium unites directly with nitrogen, forming a transparent crystallized nitride ( $Mg_3N_2$ ), which is decomposed rapidly by water into magnesia and ammonia (Deville). Geuther and Briegleb obtained a greenish yellow amorphous nitride of similar composition, by heating the metal in pure and dry nitrogen: it is immediately decomposed by water.

Magnesium reduces not only the more easily reducible metals from acidulated solutions of their salts, but also precipitates iron, zinc, nickel, and cobalt in the metallic form with evolution of hydrogen. Salts of arsenic and antimony are converted into arseniuretted and antimonuretted hydrogen; but the salts of manganese and aluminum are not reduced by it.

(684) MAGNESIA ( $MgO=40.3$ ); *Sp. Gr.* 3.6; *Comp. in 100 parts*, Mg, 60.28; O, 39.72.—The only known oxide of magnesium is a bulky, white, tasteless, infusible, and nearly insoluble powder, which when placed upon moistened turmeric-paper turns it distinctly brown. It is usually procured by strongly igniting the artificial carbonate in a crucible, but it may also be obtained by ignition of the magnesian nitrate; in this case it assumes a much denser form. Magnesia, when mixed with water, gradually combines with it, and forms a hydrate ( $H_2MgO_2$ ), which absorbs carbonic acid slowly from the air: no sensible elevation of tempe-

ture occurs during the process of hydration. A native hydrate of similar composition occurs in crystalline scales.

(685) **MAGNESIC SULPHIDE** or *Sulphide of magnesium* ( $\text{MgS} = 56.3$ ) is but sparingly soluble in water. It may be obtained as a hydrate by precipitating a boiling solution of magnesian sulphate with dipotassic sulphide, when it falls as a white mucilaginous mass.

(686) **MAGNESIC CHLORIDE**, or *Chloride of magnesium* ( $\text{MgCl}_2 = 95.3$ ; *Sp. Gr.* 2.177; *cryst. with*  $6\text{H}_2\text{O}$ , 1.562) is contained abundantly in sea water. It may be obtained in the anhydrous condition by dissolving 1 part of magnesia in hydrochloric acid, and adding 3 parts of sal ammoniac in solution, after which the mixture is evaporated to dryness; by this means a double chloride of magnesium and ammonium is formed ( $\text{H}_4\text{NCl}, \text{MgCl}_2$ ), which may be evaporated without loss of acid, whilst the solution of mere magnesian chloride is partially decomposed during evaporation: when the double salt is ignited in a covered crucible, the sal ammoniac is expelled, and pure magnesian chloride remains, which at a red heat fuses to a transparent liquid, and forms a silky-looking mass of confused crystals on cooling. Magnesian chloride is deliquescent, and gives out heat whilst undergoing solution in water; by evaporation at a low temperature it may be obtained in crystalline needles with  $6\text{H}_2\text{O}$ . It is soluble in alcohol: it forms double chlorides with the chlorides of the metals of the alkalis. If heated strongly in a current of dry ammoniacal gas, magnesian chloride is volatilized, and a white sublimate of ( $\text{MgCl}_2, 4\text{H}_3\text{N}$ ) is obtained (Clark).

*Dimagnesian oxydichloride* ( $\text{MgO}, \text{MgCl}_2$ ).—Attention has recently been called to this substance by M. Sorel, who finds that when mixed with water it possesses the remarkable property of 'setting,' like plaster of Paris (652), so that it can be applied to similar purposes; but furnishes a material much harder and more durable than ordinary plaster, and susceptible of a high polish. It may be mixed with 15 or 20 times its weight of other dry powders without losing its power of setting when mixed with a proper proportion of water.

(687) **MAGNESIC SULPHATE**, or *Sulphate of magnesia* ( $\text{MgSO}_4, 7\text{H}_2\text{O} = 120.3 + 126$ ); *Sp. Gr. anhydrous*, 2.706, *cryst.* 1.660: *Comp. in 100 parts, dry*,  $\text{MgO}$ , 33.50;  $\text{SO}_3$ , 66.50; *cryst.*  $\text{MgO}$ , 16.36;  $\text{SO}_3$ , 32.47;  $\text{H}_2\text{O}$ , 51.27.—This is the most important salt of magnesium. It is made in very large quantities from sea water, either by precipitating the magnesia by means of lime, and then dissolving it in sulphuric acid; or by first crystallizing out the greater part of the common salt, after which, on evaporation, crystals of magnesian sulphate are obtained. Native mag-

nesic carbonate is likewise sometimes acted upon with diluted sulphuric acid, and the salt obtained by evaporation. The sulphate is also procured in considerable quantities from magnesian limestone: the rock is burned, slaked, and largely washed with water to remove part of the lime; it is then treated with sulphuric acid, and the magnesian sulphate is separated from the sparingly soluble calcic sulphate by solution and recrystallization. It is also obtained in considerable quantity from the mother-liquors of the alum works. Magnesian sulphate is a common ingredient in mineral waters. Its trivial name of *Epsom salts* is derived from the circumstance of its being abundantly contained in many springs in the neighbourhood of Epsom, from the waters of which it was at one time obtained. Magnesian sulphate is soluble in 3 times its weight of water at  $59^{\circ}$  ( $15^{\circ}$  C.), and  $1\frac{1}{2}$  at  $100^{\circ}$  C. Its solution has a bitter, disgusting taste. It crystallizes readily in right rhombic prisms, which are slightly efflorescent: when heated moderately, they lose their water of crystallization; if the heat be intense and long continued, a part of the acid also escapes. If crystallized from a hot solution, oblique rhombic prisms with  $6\text{H}_2\text{O}$  are deposited, and the ordinary crystals, when heated to  $125^{\circ}\cdot6$  ( $52^{\circ}$  C.), become opaque and lose  $1\text{H}_2\text{O}$ . Crystallized magnesian sulphate loses 6 of its 7 atoms of water at a temperature below  $302^{\circ}$  ( $150^{\circ}$  C.), but it retains 1 atom even at  $392^{\circ}$  ( $200^{\circ}$  C.) This last atom may be displaced by an equivalent of an anhydrous salt, such as potassic sulphate, with which it forms a double salt, possessed of the same crystalline form as magnesian sulphate ( $\text{MgSO}_4\cdot\text{K}_2\text{SO}_4\cdot6\text{H}_2\text{O}$ ) of sp. gr. 2.076. Ammonic sulphate forms with magnesian sulphate a similar double salt.

(688) MAGNESIC NITRATE, or *Nitrate of magnesium* ( $\text{Mg}_2\text{NO}_3\cdot6\text{H}_2\text{O} = 148 + 108$ ; Sp. Gr. 1.464), is deliquescent, and soluble in alcohol; it crystallizes with difficulty.

(689) MAGNESIC CARBONATE ( $\text{MgCO}_3 = 84\cdot3$ ; Sp. Gr. 3.056) occurs native as a white, hard, amorphous mineral, called *magnésite*. It is procured artificially by precipitating a boiling solution of a magnesium salt with potassic carbonate, and dissolving the precipitate in carbonic acid water; as the gas escapes, the salt is deposited as a trihydrate, in transparent hexagonal prisms ( $\text{MgCO}_3\cdot3\text{H}_2\text{O}$ ): by exposure to air the crystals effloresce and are converted into a protohydrate ( $\text{MgCO}_3\cdot\text{H}_2\text{O}$ ). The anhydrous carbonate may be obtained by introducing a test-tube containing a solution of magnesian sulphate into a strong glass tube containing a solution of sodic carbonate, sealing the tube,

and then allowing the two solutions to mix. Crystals of magnesian carbonate are deposited slowly.

*Magnesia alba*, the common white magnesia of the shops, is made by precipitating a boiling solution of magnesian sulphate by a hot solution of sodic carbonate. The magnesian sulphate is allowed to remain slightly in excess, otherwise the precipitate contains a little sodic carbonate. It is deposited as a white, light, bulky powder, composed of hydrated magnesia ( $\text{MgH}_2\text{O}_2$ ) combined with a quantity of hydrated carbonate ( $\text{MgCO}_3, \text{H}_2\text{O}$ ), the amount of which may vary from 2 to 4 atoms to 1 atom of the hydrated magnesia; it is very sparingly soluble in water. A quantity of carbonic acid is expelled from the mixture during the preparation of this compound.

*Dolomite*, when its structure is crystalline, usually consists of magnesian and calcic carbonate in the proportion of 1 atom of each ( $\text{MgCa}_2\text{CO}_3$ ), though sometimes the proportion of calcic carbonate considerably exceeds 1 atom. A solution of calcic sulphate decomposes magnesian carbonate at ordinary temperatures, and thus spring water originally charged with calcic sulphate may, by filtration through a bed of dolomite, become impregnated with magnesian sulphate.

A very pure magnesian carbonate is manufactured from dolomite by a process introduced by Pattinson. In this operation the mineral is finely ground and sifted, and exposed to a low red heat for 2 or 3 hours, by which the magnesian carbonate is decomposed. It is then introduced into a strong iron cylinder lined with lead, where it is mixed with water, and carbonic anhydride is forced in under a pressure of 2 or 3 atmospheres, till it ceases to be absorbed; the magnesian carbonate becomes dissolved as the so-called bicarbonate, leaving the calcic carbonate: the clear liquid, when boiled, evolves  $\text{CO}_2$  and deposits the magnesian carbonate, which is drained, and dried in a stove at a low temperature.

By mixing a solution of magnesian nitrate with an excess of a saturated solution of hydropotassic carbonate, and allowing the solution to stand for some days, a remarkable double salt is deposited in regular crystals, composed of ( $\text{MgCO}_3, \text{KHCO}_3, 4\text{H}_2\text{O}$ ), but which is decomposed by redissolving it in water. The corresponding sodium salt is more stable.

A native *magnesian borate* [ $3\text{MgO}, 4\text{B}_2\text{O}_3$ ], named *boracite*, is found crystallized in cubes; it is rendered electric by heat.

(690) **MAGNESIC SILICATES.**—Silica and magnesia may be artificially combined in many proportions. A large number of minerals are formed, either wholly or partially, of magnesian sili-

cates. *Olivine* or *chrysolite*  $[2(\text{MgFe})\text{O}, \text{SiO}_2]$  is a crystallized orthosilicate, usually of a green colour, obtained from basaltic and volcanic rocks; it frequently accompanies masses of meteoric iron. *Talc* is a very soft slaty mineral, which has a formula  $[4\text{MgO}, 5\text{SiO}_2]$ . *Steatite*, *French Chalk*, or *Soapstone*, is  $(3\text{MgO}, 4\text{SiO}_2)$ . *Picrosmine* is a hydrated metasilicate,  $[2(\text{MgO}, \text{SiO}_2), \text{H}_2\text{O}]$ . *Meerschaum* is another hydrated silicate, of which the formula is  $(2\text{MgO}, 3\text{SiO}_2, 4\text{H}_2\text{O})$ . *Serpentine*  $(2[(\text{MgFe})\text{O}, \text{SiO}_2] \text{MgO}, 2\text{H}_2\text{O})$  is another hydrated magnesian silicate, in which a portion of the magnesia is often displaced by ferrous oxide. Serpentine frequently occurs in compact masses, which take a high polish, and from the beauty of its variegated colours, it is often employed for ornamental purposes. It is readily attacked by acids, and occurs in sufficient abundance to be employed as a source of the salts of magnesium.

The double magnesian silicates are still more numerous. *Augite* or *pyroxene* is one of these: it is a crystalline mineral, often found in basalt and lava, and is a silicate of calcium and magnesium, portions of which metals are often displaced by iron and manganese  $[(\text{CaMgFeMn})\text{O}, \text{SiO}_2]$ . *Hornblende*, or *amphibole* is a silicate and aluminate of magnesium, calcium, and iron, with a variable proportion of the fluorides of calcium and potassium  $[5(\text{MgCaFeMn})\text{O}, 6\text{SiO}_2, x(\text{KCaF}_2)]$ . It occurs sometimes in dark green or black crystals, at other times massive, disseminated through many rocks, such as syenite and porphyry, and frequently in basalt and lava. *Asbestos* and *amianthus* commonly consist of a fibrous variety of amphibole.

(691) PHOSPHATES OF MAGNESIUM.—*Hydro-magnesian phosphate*  $(\text{H}, \text{Mg}', \text{PO}_4, 7\text{H}_2\text{O})$ , is an efflorescent, sparingly soluble salt, which crystallizes in fine tufts of six-sided acicular prisms, when a solution of a magnesian salt is mixed with the solution of the common hydrodisodic phosphate.

*Ammonio-magnesian phosphate*  $(\text{Mg}'\text{H}_4\text{N}, \text{PO}_4, 6\text{H}_2\text{O} = 137.3 + 108)$ , or *triple phosphate*, as it was formerly called, is a more important compound than the foregoing one. It is prepared by mixing hydrodisodic phosphate, mingled with ammoniac chloride, with a magnesium salt; by agitation this compound is deposited in minute crystalline grains: it furnishes a very delicate test of the presence of magnesium: it is insoluble in water containing free ammonia, but it is taken up in appreciable quantities by pure water, and still more by solution of muriate of ammonia. It is frequently met with as a constituent of urinary calculi, both in man and in the lower animals. Ammonio-magnesian phosphate is readily soluble in

acids; ammonia precipitates it from such solutions unchanged; when ignited, it parts with its water and ammonia, and glows like alumina and zirconia as it suddenly contracts in bulk. The ignited residue contains 36.21 per cent. of  $\text{MgO}$ , and 63.79 of  $\text{P}_2\text{O}_5$ . It is frequently employed for the determination of the amount of magnesia in the course of analysis.

(692) CHARACTERS OF THE MAGNESIUM SALTS.—The salts of magnesium are colourless and have a bitter taste. Many of the magnesian minerals possess a silky lustre, and feel unctuous to the touch. Compounds of magnesium may be recognized *before the blowpipe*, by the pink tinge which they acquire when heated with cobalt nitrate.

In solution they give no precipitate with the *acid-carbonates of the alkali-metals* till boiled; but a white magnesian carbonate when mixed with *potassic* or *sodic carbonate*, unless an ammonium salt be present, which interferes with the precipitation. *Ammonic triphosphate* gives with them a white crystalline granular precipitate of ammonio-magnesian phosphate, which is easily soluble in acids. *Ammonic oxalate* mixed with sal ammoniac, gives no precipitate with the magnesian salts, neither do the *soluble sulphates*. The *fixed alkalies* throw down a white gelatinous hydrate of the earth, which is insoluble in excess of the precipitant. *Lime-water* produces a similar precipitate. *Ammonia* produces but a very incomplete precipitation of magnesia from its solutions; the gelatinous precipitate which it occasions becomes redissolved on the addition of a solution of ammoniac chloride, and a double salt of magnesium and ammonium is formed.

(693) CHARACTERS OF THE METALS OF THE FIRST GROUP (Metals of the Alkalies).—The salts of these metals when in solution are distinguished by the following characters:—1. By the absence of any precipitate on the addition of a solution of potassic or sodic carbonate: in the case of lithium, if the salt exceed two per cent. of the solution, a precipitate of lithic carbonate is liable to occur. 2. By the absence of any precipitate when sulphuretted hydrogen or ammoniac hydrosulphide is added to the solution. 3. By the occurrence of a precipitate with platinic chloride in the case of ammonium or of potassium salts;\* and by the formation of prismatic crystals of the platinic sodio-chloride when evaporated in the presence of sodium salts.

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\* Rubidium and cesium would also be found in this precipitate (607, 608), if either of these metals be present.

(694) *Estimation of Potassium and Sodium.*—If the relative proportions of the potassium and sodium be not required, their combined weight is usually ascertained in the form of sulphates. They may in most cases be readily obtained in this condition by treating the solution with sulphuric acid, evaporating to dryness, and fusing the mass in a platinum crucible in which a fragment of ammonic sesquicarbonate is suspended. The excess of sulphuric acid is thus readily dissipated, and the amount of the acid combined with the potassium and sodium, is determined by precipitation with baric chloride. When ammonium salts are present with those of potassium and sodium, the amount of ammonia may be determined by distilling it off in the manner already described (626).

In order to determine the quantity of potassium and sodium in a mixture of the salts of the two metals, they should be converted into the state of chlorides, and heated to low redness to expel moisture and all ammoniacal salts, allowed to cool, and weighed; a certain proportion of these mixed chlorides (0.7 or 0.8 grm. will suffice) is then mixed with an excess of the platinic sodio-chloride, evaporated to dryness over a steam bath, and the excess of the platinic sodio-chloride removed by washing with alcohol of specific gravity 0.860. The crystalline residue is collected on a filter and weighed. One hundred parts contain 30.53 of potassic chloride, and correspond to 16.02 of potassium, or to 19.29 of anhydrous potash. The quantity of sodic chloride is obtained by deducting the weight of the potassic chloride from that of the mixed chlorides employed.

(695) *The conversion of the alkali-metals into the condition of chlorides*, previous to precipitation by the platinic chloride, if they are not already in that form, is rather troublesome. They may be first changed into sulphates by evaporating the solution with a slight excess of sulphuric acid, and igniting the residue; the sulphates thus obtained are to be dissolved in water and mixed with a solution of baric chloride in slight excess. The sulphuric acid is thus precipitated as baric sulphate, and the alkalies are converted into chlorides; but the excess of barium in the liquid must still be got rid of. A mixture of caustic ammonia and ammonic sesquicarbonate is therefore added to the solution after it has been filtered from the baric sulphate. The excess of barium is thus thrown down as carbonate, and the baric carbonate may then be removed by filtration. Once more the solution is to be evaporated to dryness in a platinum dish, and the residue gently ignited to expel the ammoniacal salts. The remaining



mass now contains nothing but the mixed sodic and potassic chlorides.

(696) **CHARACTERS OF THE METALS OF THE SECOND GROUP** (Metals of the Alkaline Earths, including Magnesium):—1. The salts of these metals when in solution give a white precipitate on the addition of solution of sodic or potassic carbonate.—2. They yield no precipitate with ammoniacal hydrosulphide nor with sulphuretted hydrogen.—3. Lime-water occasions no precipitate, except in cases in which magnesium salts are present, or in which the solution contains free carbonic acid.

(697) *Separation of the Alkaline Earths from the Alkalies.*—Supposing a solution to contain salts of the alkalies and of the alkaline earths, the quantities of each base may be determined in the following manner:—An excess of a mixture of ammonia and ammoniacal sesquicarbonate is added to the solution; the ammonium thus combines with the radicle of the acid previously in union with the earths, whilst the carbonic acid converts the earths into carbonates; the liquid is filtered from the precipitate, then evaporated to dryness, and heated to expel the ammoniacal salts. The dry residue is afterwards washed with water, which dissolves out the salts of the alkali-metals: and from this liquid the proportions of potassium and sodium can be ascertained in the manner already described (694). A little magnesia is apt to accompany the salts of the alkali-metals: its presence may be detected and its quantity determined by the addition of lime-water to the solution; hydrated magnesia is precipitated, and may be collected, weighed, and added to the amount obtained from the portion which was precipitated as carbonate. The precipitation must be effected in a stoppered bottle, to exclude the carbonic acid of the atmosphere, which would precipitate a portion of lime with the magnesia. The excess of lime may be got rid of by the addition of oxalic acid, which occasions a precipitate of calcic oxalate that can be separated on a filter, but need not be weighed. The earthy carbonates must now be dealt with in the following manner:—

(698) *Separation of Barium, Strontium, Calcium, and Magnesium from each other.*—The alkalies having been separated in the manner just described, the carbonates of the metals which in the preceding operation were not dissolved by water are taken up with diluted nitric acid, and the liquid is largely diluted. Sulphuric acid is then added so long as it occasions a precipitate.

If the liquid originally contained no alkaline salts, it will not be necessary to convert the earths into carbonates, but the solu-

tion may be simply diluted, acidulated with nitric acid, and mixed with sulphuric acid, as before.

This precipitate may consist of baric and strontic sulphates. It must be collected, washed with boiling water and weighed, then fused with thrice its weight of sodic carbonate, by which it will be decomposed; double decomposition occurs, baric and strontic carbonates and sodic sulphate being formed. The baric and strontic carbonates, being insoluble, are separated from the soluble sodic sulphate by washing, and the carbonates of the two earths are converted into chlorides by the action of diluted hydrochloric acid. The baric and strontic chlorides are evaporated to dryness, weighed, and may then be separated with tolerable exactness by the action of alcohol, which dissolves the strontic chloride, but leaves the barium salt unacted upon. Hydrofluosilicic acid may also be employed to separate the two earths; in the course of two or three hours the whole of the barium is precipitated by it, whilst the strontium remains in solution.

The acid liquid from which the barium and strontium have been separated is rendered slightly alkaline by ammonia, and the calcium precipitated as oxalate, by means of ammonic oxalate: this precipitate, after being well washed, is heated to dull redness, and is estimated as calcic carbonate. If the proportion of magnesium be large, a little of the calcium salt is retained in solution.

The filtrate, which may still contain magnesium, is mixed with hydrodisodic phosphate, briskly stirred, and allowed to stand for twelve hours, to give time for the granular crystalline ammonio-magnesian phosphate to subside: it is collected on a filter, washed with water which contains free ammonia, and estimated, after ignition, as magnesian pyrophosphate.

It will generally be found more convenient in separating the metals of the alkaline earths from those of the alkalis, in the first place to precipitate the barium and strontium by sulphuric acid from the dilute acidulated solution; then to neutralize by ammonia, and separate the calcium by the addition of ammonic oxalate; to evaporate the solution containing the salts of magnesium and of the metals of the alkalis to dryness, heating, to expel salts of ammonium; then to redissolve the residue in water, and separate the whole of the magnesia at once by the addition of lime-water in a stoppered bottle, in the manner already described.

(699) *Collection of precipitates.*—Certain precautions in manipulation are required in transferring a solution to a filter, in order to avoid loss. In pouring

a liquid from one vessel to another, a glass rod should be moistened with distilled water and brought against the edge of the vessel from which the liquid is to be poured, as shown in fig. 350. By this means, when the pouring is ended, if the rod be still kept in contact with the edge, the last drop is prevented from running down the outside of the jar or basin: the rod may then be placed in the vessel until a similar operation is again required. After the whole of the liquid has been poured off, the portion which adheres to the rod and to the sides of the vessel is washed down by a jet of water from the washing bottle, fig. 351, and the washings are added to the rest of the decanted liquid.

FIG. 350.



(700) *Washing of Precipitates.*—

In washing precipitates, the use of a flask provided with two tubes passing through the cork, as represented in fig. 351, facilitates the operation. The

FIG. 351.



tube *a*, passes just through the cork; the longer tube, *b*, reaches almost to the bottom of the flask; it terminates at *c* in a fine orifice; on forcing air from the lungs through the tube *a*, the water is expelled at *c*, and may be directed upon the filter.

It is necessary that the filter should fall completely within the funnel, and that before any of the liquid for filtration is poured into it, the paper, after it has been placed in the funnel, should be moistened with distilled water. In washing a precipitate, the stream of water should be directed upon the upper edges of the filter, so as to wash down the saline particles, which, by evaporation of the liquid, have a tendency to accumulate there as the solution rises under the influence of capillary action.

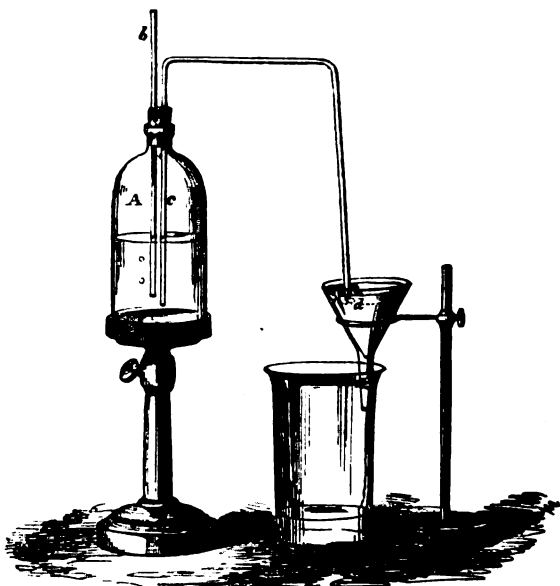
In cases where gelatinous precipitates, like hydrated oxide of iron or alumina, are to be washed continuously for a long period, a simple contrivance by Gay-Lussac will be found very useful; it is merely a bottle of distilled water, *A*, fig. 352, which by means of a siphon, supplies the water at a regulated level in the funnel, *d*; *b* represents a tube open at both ends, which reaches nearly to the bottom of the bottle, *A*; *c* is a siphon with limbs of equal length, which passes a little deeper into the bottle than *b*; the limb which dips into the funnel has its lower extremity a little recurved, to direct the pure water upwards, and the siphon can be filled by blowing gently into the bottle through the tube *b*. The funnel, *d*, is placed so that the upper edge of the filter shall be a little above the level of the lower end of *c*. Under these circumstances the filter can never overflow. As soon as the surface of the liquid in the funnel falls just below the level of the lower extremity of *b*, the siphon carries over a small quantity of water, and bubbles of air rise in the bottle, *A*, to supply its place. This process goes on continuously as the water flows from the filter, until *A* is empty.

In order to ascertain whether a precipitate has been sufficiently washed, a drop of the liquid which passes through is evaporated on a slip of glass: it ought to leave no appreciable stain or residue.

In collecting a precipitate from a filter, the paper should be dried thoroughly; after which the portion that can be readily detached from the paper should be

allowed to fall into the platinum or porcelain capsule in which it is intended to perform the ignition. The capsule is to be placed upon a smooth sheet of paper, and the filter being held at one corner with a pair of forceps, or suspended in a coil of platinum wire, is burned in such a way that the ashes shall fall into the platinum capsule: any particles of ash which may fall upon the paper are carefully transferred to the capsule.

FIG. 352.



It must not be forgotten that filtering-paper itself leaves traces of ash when burnt; but the amount of this in good specimens should not exceed about 3 grains in 1000. Before using any paper for the purposes of analysis, the quantity of ash (usually consisting of silica, lime, and traces of ferric oxide) which a given weight of it affords when burnt must be ascertained. In each analytical experiment the weight of the filter employed being approximatively known, it is easy to estimate the amount of ash which it would yield (at most but a few hundredths of a grain) and to deduct this from the gross weight of the precipitate.\*

§ II. ZINC: ( $Zn''=65.0$ .) *Sp. Gr.* 6.8 to 7.1; *Fusing-pt.*  $773^{\circ}$  ( $412^{\circ}$  C.); *Boiling-pt.*  $1904^{\circ}$  ( $1040^{\circ}$  C.); *Atomic and Mol. Vol. of Vapour*,   ; *Rel. wt.* 65.

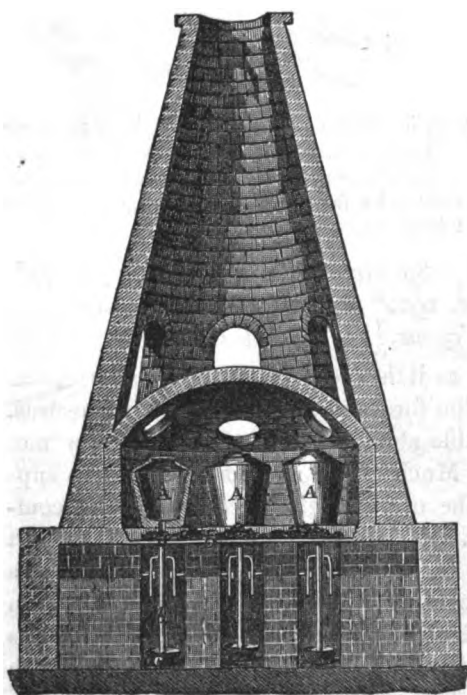
(701) ZINC, or *spelter*, as it is often called in commerce, has been known in the metallic form since the time of Paracelsus. Its ores occur in considerable abundance, though it is never met with in the native state. Much of the zinc of commerce is supplied from Silesia, where the ore wrought is *calamine*; the common or rhomboidal calamine (zincic carbonate) is the most important variety, though the prismatic or electric calamine, a hydrated basic zincic silicate, is found often in the Carinthian ores: it is much more difficult of reduction. Zincic carbonate is also extensively worked in Belgium, where it is found mixed with

\* In delicate inquiries it is desirable first to wash the filter with dilute nitric acid (1 of acid to 30 of water), by which nearly everything, except the silica, is removed, then washing well with distilled water.

clay. In the Mendip Hills, in Somersetshire, the zincic carbonate is associated with magnesian limestone. *Blende*, or zincic sulphide, is worked in England to some extent; it usually accompanies plumbic sulphide (or galena) in the mountain limestone. In New Jersey *red oxide of zinc* has been found in large quantities both massive and crystallized; the colour is due to admixture with oxides of manganese and iron. It forms a valuable ore, and is easily reduced. In the year 1860, 4357 tons of zinc were extracted from English mines.

(702) *Extraction of Zinc from its Ores.*—In the extraction of zinc, whether from blende or from calamine, the ore is crushed between rollers, and undergoes a process of roasting; in the case of blende a preliminary mechanical treatment is required, in order to separate the galena as completely as possible, as the presence of lead would occasion rapid destruction of the crucibles during the subsequent reduction of the metal. The roasting of blende is tedious, and requires to be carefully performed; the

FIG 353.



sulphur burns away as sulphurous anhydride, and the zinc becomes oxidized;  $2\text{ZnS} + 3\text{O}_2$  yield  $2\text{ZnO} + 2\text{SO}_2$ . Calamine also yields zincic oxide when roasted, whilst carbonic anhydride and water are expelled. The roasted ore from either source is mixed with half its weight of powdered coke or anthracite, and introduced into crucibles of peculiar construction.

The method of reduction practised in England offers one of the few instances in which distillation *per descensum* is still practised:—a circular furnace, somewhat similar to that used in making glass, is employed: in this furnace six large clay crucibles, (three of which are re-

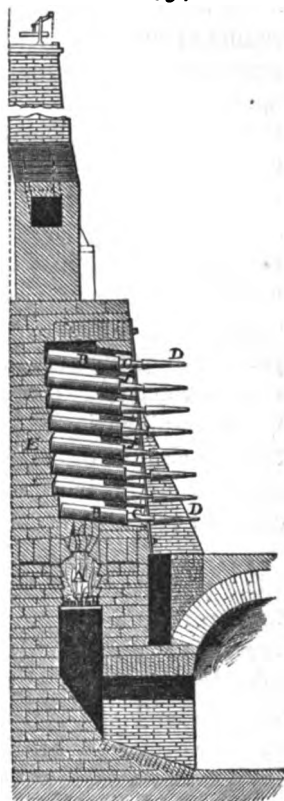
presented in the section at A, A, A, fig. 353,) each 1·22 metres or 4 feet high and 0·76 metre or 2½ feet in diameter, are arranged, three on each side of the

firebars; one of these crucibles is shown in section in the figure. In the bottom of each crucible is an opening, and to this is attached a short iron pipe, which passes out through the bottom of the furnace; to this iron tube a second wider tube, *b*, about 2·44 metres or eight feet long, is fastened in such a manner as to be readily removeable; beneath the open end of this tube a sheet-iron vessel, *c*, is placed to receive the zinc. The bottom of the crucible is then loosely plugged with large pieces of coke, and a charge containing from 200 to 250 kilos. (from 4 to 5 cwt.) of the mixture of calcined ore and coal is introduced into each pot, and the cover is carefully luted on. Carbonic oxide is first evolved abundantly, and burns with a blue flame at the mouth of the short iron tube; in a few hours the colour of the flame changes to brown, when the cadmium, which is more volatile than zinc, comes over, and may be condensed. When the colour of the flame changes to bluish-white, the zinc is distilling nearly pure. The flame is then extinguished by attaching the longer tube, and the metal becomes condensed partly in powder, partly in stalactitic masses, and falls down into the iron vessels, *c, c*, placed for its reception. The zinc, being volatile at very high temperatures, boils and distils as the operation proceeds. In order to prevent the pipe, *b*, from becoming choked, it is occasionally removed, and the zinc detached from it. The crude metal is mingled with a good deal of oxide: it is therefore re-melted, skimmed, and cast into ingots; or (if intended for rolling) into sheets, and then laminated at a temperature of about 248° (120° C.). Calamine, which contains 52 per cent. of metal, does not yield on an average above 30; the greater part of the zincic silicate, which calamine almost always contains, escaping decomposition.

(703) In Silesia the distillation is effected in muffle-shaped earthen retorts, which are ranged in two rows on the same plane in a long furnace, back to back: the outer end of each retort is provided with two apertures; the lower one is employed for introducing the charge, and is afterwards carefully luted up, whilst the upper one is for receiving a bent earthen pipe which carries off the metal as it distils.

(704) In Belgium the distillation is managed quite differently. The ores treated in that country are of two kinds, both occurring in a matrix of clay above a bed of dolomite: one is a red variety, containing about 33 per cent. of zinc, with a good deal of oxide of iron, but admitting of reduction at a moderate temperature; the other is a white ore, also a calamine, which contains about 46 per cent. of zinc, and requires a much higher temperature for its reduction. These two species of ore are kept distinct from each other during the process of smelting. The calamine, having been washed to remove the clay, is roasted, during which operation it loses about 25 per cent. of water and carbonic anhydride. After this it is reduced to a fine powder, and thoroughly mixed with half its weight of coal dust: this mixture is then introduced into clay retorts about three feet eight inches (1·1 metre) long and six inches or 15 centimetres in diameter; each retort is charged with about 40 lb. or 18 kilos. of the mixture

FIG. 354.



of coal and roasted ore. Forty-two of these retorts are arranged in an arched furnace, in rows of six, placed one above another. The backs of the retorts rest on notches in the wall, *E*, fig. 354, and are supported on a slightly higher level than the open extremities, which rest in front upon iron plates, *f*, *f*. To each retort an open, somewhat conical, cast-iron pipe, *c*, is luted; this serves as a receiver for the distilled metal, and upon each of these receivers is fitted a second receiver of sheet iron, *D*, with an opening at the extremity for the escape of gas. The fire by which the retorts are heated is shown at *A*. In such a furnace two charges may be worked off in twenty-four hours. During the operation the small adapters, *D*, *D*, are withdrawn once in two hours, and the liquid zinc which has condensed in the receivers is raked out into a large ladle and cast into ingots. When the distillation is complete, the residues in the retorts still retain nearly 25 per cent. of zinc, which is chiefly in the form of silicate; this portion is entirely wasted (Piot and Murailhe, *Ann. des Mines*, IV. v. 165).

The retorts in the upper part of such a furnace necessarily receive less heat than those in the lower part, and hence this process is particularly well adapted to the Belgian ores, because the poorer ones, which require less heat, can be employed in charging the upper retorts.

(705) *Preparation of pure Zinc*.—Commercial zinc contains a small amount of lead and of iron; minute quantities of tin and cadmium are also often present, besides occasionally traces of arsenicum and of copper. Carbon is also mentioned among its impurities, but Eliot and Storer, in their elaborate examination of the ordinary impurities of this metal, did not find it in any of the 13 specimens which they examined, though traces of sulphur were always present. The best method of obtaining the metal in a state of purity consists in transmitting sulphuretted hydrogen through a strong and somewhat acid solution of zincic sulphate, filtering from any precipitate which may be formed; and after boiling the solution, in order to expel the sulphuretted hydrogen, precipitating the zinc in the form of carbonate by the addition of sodic carbonate. The carbonate is to be washed and redissolved in pure sulphuric acid and submitted to electrolytic decomposition, or else the dried carbonate may by ignition be converted into zincic oxide, which must be distilled in a porcelain retort with charcoal prepared from loaf sugar.

(706) *Properties*.—Zinc is a hard, bluish-white metal, which, when a mass of it is broken across, exhibits a beautiful crystalline fracture. It is rather brittle at ordinary temperatures, but between  $212^{\circ}$  and  $302^{\circ}$  ( $100^{\circ}$  and  $150^{\circ}$  C.), it is possessed of considerable ductility and malleability, and it may be laminated and wrought with ease: at a temperature a little higher than this, it again becomes so brittle that it may be pulverized in a mortar. It fuses at about  $773^{\circ}$  ( $412^{\circ}$  C.), and at a bright red-heat it may be volatilized: the temperature of its boiling-point is estimated by Deville at  $1904^{\circ}$  ( $1040^{\circ}$  C.): if its vapour be exposed to the air,

it burns with great splendour and is converted into oxide, which is deposited in copious white flocculi. Zinc soon tarnishes when exposed to a moist atmosphere, and becomes covered with a thin, closely-adhering film of oxide, by which the metal beneath is protected from further change. This property renders zinc valuable for a variety of economical and domestic purposes. It combines, however, readily at ordinary temperatures with chlorine, bromine, and iodine, if moistened with water; it is also easily attacked by all the mineral acids, and is employed to decompose diluted sulphuric acid when hydrogen is required. A strong solution of potash likewise acts upon zinc if boiled upon it; hydrogen being liberated, whilst the zinc is dissolved in the alkaline solution;  $\text{Zn} + 2\text{KHO}$  becoming  $\text{H}_2 + \text{K}_2\text{O}, \text{ZnO}$ . Zinc precipitates most of the basylous metals less oxidizable than itself in the metallic state from their solutions.

(707) *Uses*.—The uses of zinc are daily extending. From its durability, cheapness, and lightness, it is frequently employed as a substitute for lead in roofing. It is employed as the oxidizable metal in the construction of the voltaic battery. Sheet iron coated with zinc, or *galvanized* iron as it is often called, is also used for roofing; the iron gives strength, whilst the zinc protects it from oxidation, and it is not combustible like zinc alone. Galvanized iron is prepared by cleaning sheet iron thoroughly as in making tin-plate (811), and plunging the metal into a bath of molten zinc, covered with sal ammoniac; the surface of the zinc is by this means kept free from oxide, which is dissolved by the sal ammoniac, and the two metals unite readily. A tougher and superior article is obtained by first coating the iron plate with a very thin film of tin by a voltaic action, and then immersing the metal in the melted zinc.

Zinc has a considerable power of dissolving iron, in consequence of which it corrodes the iron pots in which it is melted: an alloy of zinc with a small proportion of iron is formed, which is less fusible than zinc, and crystallizes in large plates on cooling.

Zinc forms several valuable alloys. Of these, brass is the most important: it consists of about 2 parts of copper to 1 of zinc. German silver is brass containing a portion of nickel, to which its white colour is due. Of late years zinc in powder has been employed as the basis of a pigment well adapted to resist the action of the weather. Zincic oxide has likewise been substituted for red lead with advantage in the preparation of glass for optical purposes (599).

(708) ZINCIC OXIDE, or *Oxide of zinc* ( $\text{ZnO} = 81$ ); *Sp. Gr.*



5·612 : *Comp. in 100 parts*, Zn, 80·24 ; O, 19·76.—It is possible that the film which is formed upon the surface of metallic zinc by exposure is a suboxide ; but only one well ascertained oxide of the metal is known, and this is regarded as a protoxide : this oxide is occasionally deposited in furnace flues in yellowish six-sided prisms ; but it is generally obtained in the form of a white flocculent powder. If zinc be thrown in small quantities at a time into a capacious clay crucible previously heated to whiteness, it burns with a brilliant flame and deposits large white flakes of the oxide ; but when thus prepared, it is mechanically mixed with particles of the metal, from which it may be separated by levigation with water ; the heavier metallic portions subside quickly and leave the oxide in suspension. The process of manufacturing this oxide when it is required as a pigment, known as *zinc white*, consists in distilling zinc from clay retorts into chambers through which a current of air is maintained. The volatilized metal burns at the high temperature to which it is exposed under these circumstances, and the oxide is deposited in a series of condensing chambers. It has been attempted to introduce this white pigment as a substitute for white lead, but though the colour is permanent, and of a pure white, it does not combine chemically with the oil necessary as a vehicle for distributing the colour, and hence it soon peels off, and allows moisture to penetrate. An impure oxide, sold under the name of *tutty*, is obtained from the flues of furnaces in which brass is melted.

Zincic oxide becomes yellow when heated, but recovers its whiteness as the temperature falls. It is readily soluble in acids. The hydrated oxide ( $\text{ZnH}_2\text{O}_3$ ) is precipitated from the solutions of the salts of zinc by the addition of potassic or sodic hydrate, as well as by ammonia ; it is redissolved by an excess of the alkaline liquid.

(709) ZINCIC SULPHIDE, *Sulphide of zinc*, or *Blende* ( $\text{ZnS}=97$ ) ; *Sp. Gr.* 4·1 ; *Comp. in 100 parts*, Zn, 67·01 ; S, 32·99.—This compound is one of the most abundant minerals of zinc. When pure it is of a pale-brown colour, but generally it is nearly black from admixture with sulphide of iron. It sometimes occurs massive, but is usually crystallized in rhombic dodecahedra, though it occurs in other forms of the regular system. Metallic zinc does not unite readily with sulphur : but if heated rapidly in mixture with cinnabar (mercuric sulphide), the mercury is volatilized, and zincic sulphide is formed with almost explosive violence. Zincic sulphide does not fuse when heated : when roasted in the air it absorbs oxygen ; at a low temperature a large portion of it

is converted into zincic sulphate, but at a higher temperature sulphurous anhydride is formed, and zincic oxide is left. The sulphide is only slightly attacked by sulphuric and hydrochloric acids, but nitric acid and aqua regia dissolve it readily. When the salts of zinc are mixed with hydro-ammonic sulphide, a white, gelatinous, hydrated zincic sulphide is precipitated, which absorbs oxygen quickly from air, and is readily dissolved by acids.

(710) ZINCIC CHLORIDE, or *Chloride of zinc* ( $\text{ZnCl}_2 = 136$ ); *Sp. Gr.* 2.753.—This salt may be procured by heating the metal in chlorine gas, but it is generally obtained by dissolving the metal in hydrochloric acid; the acid is decomposed, its chlorine unites with the zinc, forming zincic chloride, which is retained in solution, whilst its hydrogen escapes in the gaseous form. When this solution is heated, it loses water till the temperature rises to  $482^\circ$  ( $250^\circ \text{C.}$ ); it then becomes anhydrous, but remains fluid, and may be heated to above  $700^\circ$  ( $371^\circ.2 \text{C.}$ ) without emitting an inconvenient amount of fumes; hence it is sometimes employed as a hot-bath for maintaining objects at a high but measurable and regulated temperature. At a red heat it distils. Pure zincic chloride is a white, very deliquescent substance, fusible at about  $100^\circ \text{C.}$ ; it is powerfully corrosive when applied to the skin. Under the name of *Burnett's Disinfecting Fluid*, its solution has been largely used as an antiseptic, and as a preservative of wood and vegetable fibre against decay. Zincic chloride is soluble in alcohol.

Zincic chloride absorbs ammoniacal gas freely. It also unites with zincic oxide in several proportions, and forms a number of oxychlorides. Zincic chloride forms double salts with the chlorides of the alkali-metals; a concentrated solution of zinc-ammonic chloride ( $2\text{H}_4\text{NCl}, \text{ZnCl}_2$ ) is used for the purpose of removing the film of oxide from the surface of metals, such as zinc, iron, or copper, which are to be united by the operation of soldering.

(711) ZINCIC SULPHATE, or *Sulphate of zinc* ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} = 161 + 126$ ); *Sp. Gr.*, anhydrous, 3.681; *cryst.* 1.931, is obtained in large quantities as a residue in the ordinary process of procuring hydrogen by the action of diluted sulphuric acid. It may also be prepared by roasting zincic sulphide at a low temperature, lixiviating the mass and crystallizing. It crystallizes in colourless four-sided prisms, which constitute the *white vitriol* of commerce. In a dry air it is efflorescent; it is soluble in  $2\frac{1}{2}$  parts of water at  $59^\circ$  ( $15^\circ \text{C.}$ ), and melts in its water of crystallization when heated; it may be obtained crystallized with 6, 5, 2, and 1 atom of water, by varying the temperature at which the crystals

are allowed to be formed. Zincic sulphate is used medicinally in small doses ; it is likewise prepared largely for the calico printer. It forms double sulphates with potassium and with ammonium, which crystallize with  $6\text{H}_2\text{O}$ . Several basic zincic sulphates may also be obtained.

(712) **ZINCIC CARBONATE**, or *Carbonate of zinc* ( $\text{ZnCO}_3 = 125$  ; *Sp. Gr.* 4.4 ; *Comp. in 100 parts*,  $\text{ZnO}$ , 64.8 ;  $\text{CO}_2$ , 35.2 ; or  $\text{Zn}$ , 52 ;  $\text{CO}_2$ , 48), is found native, both massive and crystallized, in forms derived from the rhombohedron. It is usually of a greyish or yellowish colour, forming one variety of *calamine*, which is so named from its property of adhering, after fusion, in the form of reeds, to the base of the furnace. It readily loses carbonic anhydride when ignited. No neutral zincic carbonate can be obtained from the salts of the metal by double decomposition. When a hot solution of a zincic salt is precipitated by a boiling solution of an alkaline carbonate, a hydrated oxycarbonate is formed, consisting of  $(8\text{ZnO}, 3\text{CO}_2, 6\text{H}_2\text{O})$  ; Schindler). Several other basic zincic carbonates may be formed.

The other variety of calamine becomes electric by heat ; it is a hydrated orthosilicate  $(2\text{ZnO}, \text{SiO}_2, \text{H}_2\text{O})$ .

(713) **CHARACTERS OF THE SALTS OF ZINC.**—The zinc salts are colourless ; their solutions have an astringent, metallic taste, and act rapidly and powerfully as emetics.

They are distinguished by giving no precipitate in acid solutions with *sulphuretted hydrogen*, though the acetate, even when acidulated with acetic acid, gives a white hydrated sulphide when the gas is transmitted : they yield a white hydrated sulphide of zinc with *hydro-ammonic sulphide*, a white hydrated oxide with caustic *potash*, *soda*, or *ammonia*, soluble in excess of the alkali ; a white basic zincic carbonate with the *carbonates of the alkali-metals*, soluble in excess of the solution of ammonic carbonate, but not in that of potassic or sodic carbonate ; they also yield a white precipitate with *potassic ferrocyanide*.

*Before the blowpipe*, in the reducing flame on charcoal, the metal is reduced and volatilized, burning into white fumes of zincic oxide. If placed on charcoal and moistened with a solution of cobalt nitrate, the compounds of zinc when heated in the oxidating flame leave a green residue, which is not fusible.

(714) **Estimation of Zinc.**—Zinc is best precipitated for analysis by potassic carbonate, the whole solution being evaporated down to dryness ; the residue, which contains the zincic carbonate, is washed with boiling water, dried, and converted by ignition into

zincic oxide, which is weighed. The oxide contains, in 100 parts, 80.24 of zinc. If ammoniacal salts be present, an excess of the potassic carbonate should be used sufficient to decompose the ammoniacal salts completely, the ammonia being wholly expelled as carbonate during the process of evaporation. The foregoing process is not applicable to the separation of zinc from any but the alkali-metals.

(715) *Separation of Zinc from the Alkalies and Alkaline Earths.*

—This may be effected by the addition of hydro-ammonic sulphide to the solution after it has been neutralized by ammonia; the zinc is thus precipitated as hydrated sulphide: it must be washed with a solution of sulphuretted hydrogen, to prevent its oxidation, then redissolved in hydrochloric acid, and evaporated to dryness with excess of potassic carbonate: the soluble salts must be washed from the zincic carbonate, which is to be converted into oxide by ignition, and then weighed.

*The separation of zinc from aluminum and glucinum* may be effected by dissolving all the bases by means of an excess of caustic potash, and adding hydro-ammonic sulphide: in this case zincic sulphide is alone precipitated: it may be collected and its amount determined in the manner just described.

§ III. CADMIUM: ( $\text{Cd}'' = 112$ ); *Sp. Gr.* 8.6 to 8.69; *Fusing-pt.*  $442^{\circ}$  ( $227^{\circ} 8 \text{ C.}$ ); *Boiling-pt.*  $1580^{\circ}$  ( $860^{\circ} \text{ C.}$ ); *Theoretic Sp. Gr. of vapour*, 3.869; *Observed*, 3.94; *Atomic and Mol. Vol. of Vapour*,   ; \* *Rel. wt.* 56.

(716) CADMIUM was discovered by Stromeyer, in 1818. It is occasionally found as cadmic sulphide, accompanying the ores of zinc, and is obtained as an accidental product during the extraction of the latter metal. Being more volatile than zinc, the greater part of the cadmium sublimes among the first portions of the distilled metal, from which it may be extracted by dissolving them in sulphuric acid, and precipitating the cadmium as sulphide by means of sulphuretted hydrogen: the sulphide may be dissolved in strong hydrochloric acid, precipitated by ammoniac sesquicarbonate, and reduced in an earthen retort by ignition with charcoal; the metal distils over at a heat below redness.

Cadmium is of a white colour, resembling tin, and, like it, creaks when a rod of it is bent; it is so soft that it leaves its

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\* This vapour (as well probably as that of zinc and the other metallic dyads, is anomalous in volume, 1 atom of each metal yielding 2 volumes instead of 1 volume.

traces upon paper, and possesses considerable malleability and ductility; when heated to about  $176^{\circ}$  ( $80^{\circ}$  C.), it becomes very brittle, and may be powdered in a mortar with facility. Cadmium fuses at  $442^{\circ}$  ( $227^{\circ}.8$  C.), and may be obtained in octohedral crystals as it cools. In the atmosphere it undergoes little change, but when thrown into a red-hot crucible it takes fire, depositing brownish-yellow fumes of oxide. It is dissolved with evolution of hydrogen when heated in sulphuric or hydrochloric acid slightly diluted; nitric acid dissolves it still more freely.

The addition of cadmium to the more fusible metals generally yields an alloy of low fusing-point, without destroying the toughness or malleability of the compound. An alloy consisting of 15 parts of bismuth, 8 of lead, 4 of tin, and 3 of cadmium, furnishes a silver-white alloy of sp. gr. 9.4: it softens between  $131^{\circ}$  and  $140^{\circ}$  ( $55^{\circ}$  and  $60^{\circ}$  C.), and at about  $60^{\circ}$  C. is completely liquid; it expands a little as it solidifies. This alloy is somewhat ductile, and may be filed readily without clogging the tool; it preserves its brilliancy in the air. An alloy consisting of 1 part of cadmium, 6 parts of lead, and 7 of bismuth, melts at  $179^{\circ}.6$  ( $82^{\circ}$  C.).

(717) **CADMIC OXIDE**, or *Oxide of cadmium* ( $\text{CdO} = 128$ ); *Sp. Gr.* 6.93; *Comp. in 100 parts*, Cd, 87.5; O, 12.5.—This oxide is obtained as a brown anhydrous powder, by burning the metal in air, or by igniting cadmic nitrate; it is not fusible or volatile in the furnace. A white hydrated cadmic oxide  $\text{CdO}, \text{H}_2\text{O}$ , may be obtained by decomposing its salts by a fixed alkali; ammonia in excess redissolves it, but the potassic and sodic hydrates have no such effect; even the anhydrous oxide is soluble in ammonia. Ammoniac sesquicarbonate does not dissolve cadmic oxide either in the anhydrous or the hydrated form.

**CADMIC SULPHIDE** ( $\text{CdS} = 144$ ) constitutes the mineral known as *greenockite*, which occurs crystallized in six-sided prisms. It may be formed artificially by transmitting a current of sulphuretted hydrogen through a solution of a salt of cadmium; it greatly resembles orpiment in appearance, but is distinguished from it by its want of volatility when heated, and by its insolubility in ammonia and in the sulphides of the alkali-metals. It forms a bright yellow pigment highly valued both for the purity and permanence of its tint.

**CADMIC CHLORIDE**, or *Chloride of cadmium* ( $\text{CdCl}_2, 2\text{H}_2\text{O}$ ) crystallizes easily. The *iodide* (sp. gr. 4.576) may be also obtained without difficulty in crystals which have a pearly lustre. It is anhydrous, and fuses readily on the application of heat. This salt is easily obtained by digesting metallic cadmium in water with free iodine, and evaporating the solution; it is employed for iodizing collodion for photographic purposes (1274).

(718) **CHARACTERS OF THE SALTS OF CADMIUM.**—The cadmic salts are colourless, and resemble those of zinc. They may be readily distinguished by the yellow precipitate of cadmic sulphide which they yield with *sulphuretted hydrogen* in acid solutions; this precipitate is insoluble either in ammonia or in the alkaline sulphides, or in potassic cyanide, but soluble in boiling diluted

sulphuric acid. *Caustic potash and soda* give a precipitate of white hydrated oxide, insoluble in excess of the precipitant; *ammonia*, a similar precipitate very soluble in excess; *carbonates of potassium, sodium, and ammonium*, a white carbonate, insoluble in excess; *oxalic acid*, a white precipitate, soluble in ammonia; *potassic ferrocyanide*, a yellowish-white precipitate, soluble in hydrochloric acid.

*Before the blowpipe* they are decomposed, and on the cool part of the charcoal a ring of brown cadmic oxide is deposited, due to the reduction and subsequent combustion of the metal.

*Estimation of Cadmium.*—Cadmium is readily separated from all the foregoing metals by the action of sulphuretted hydrogen, which causes a precipitate of yellow cadmic sulphide from an acidulated solution of the salts of this metal. This precipitate is redissolved in nitric acid, decomposed by an excess of sodic carbonate, evaporated to dryness, washed from the soluble salts, and the resulting cadmic carbonate is heated to redness, by which it is converted into oxide; it is then weighed: 100 grains of cadmic oxide contain 87.5 of the metal.

## CHAPTER XVI.

### GROUP V.—METALS MORE OR LESS ALLIED TO IRON.

Metals.	Symbol.	Atomic weight.	Atomic vol.	Specific heat.	Specific gravity.	Electric conductivity °C.
Cobalt ...	Co	59	6.94	0.1069	8.950	17.22
Nickel ...	Ni	59	6.94	0.1086	8.820	13.11
Uranium ...	U	120				
Iron ...	Fe	56	7.10	0.2138	7.844	16.81
Chromium ...	Cr	52.5	7.00		6.810	
Manganese ...	Mn	55	7.00	0.1217	8.013	

THE metals of this class include those which are distinctly magnetic; uranium, however, appears to be diamagnetic. They decompose water at a red heat, and are soluble with evolution of hydrogen in hydrochloric and diluted sulphuric acid. They form several oxides, two at least of which, except in the case of cobalt and nickel, are soluble in acids. Sulphuretted hydrogen in solutions acidulated with the mineral acids does not precipitate the metals of this group. Corresponding salts of these metals are isomorphous (see page 331).

§ I. COBALT: ( $\text{Co}^{\sim} = 59$ ). *Sp. Gr.* 8.95.

(719) COBALT appears to have been first recognized as a distinct metal by Brandt, in 1733. It generally occurs in com-

bination with arsenic, as speiss-cobalt or tin-white cobalt ( $\text{CoAs}_2$ ), but occasionally it is found as cobalt glance, which is a compound of the arsenide and the sulphide of the metal ( $\text{CoSAs}$ ). Cobalt is never met with in the native state, except as an ingredient in meteoric iron in small proportions. The black oxide has been found to some extent in the Western States of America, mixed with cobalt sulphide, and with variable proportions of the oxides of nickel, manganese, iron, and copper. The ores of this metal occur chiefly in the primitive rocks, and are usually very complicated; they contain nickel, iron, and often bismuth and copper, mineralized either by sulphur or by arsenic, or by both together.

*Extraction.*—It is not easy to obtain cobalt in a state of purity. On a small scale the ore may be treated as follows:—It is first roasted at a low but gradually rising temperature, in order to expel the greater portion of the arsenic: after which it is dissolved in aqua regia, and evaporated to dryness to drive off the excess of acid; it is then redissolved in water, and a current of sulphuretted hydrogen is transmitted through the solution. Bismuth, copper, and the remainder of the arsenic are thus precipitated as sulphides. The filtered liquor is boiled to expel the excess of the gas, and a slight excess of nitric acid is added to the boiling liquid, to convert the ferrous into ferric salts; when cold, it is diluted and supersaturated with ammonia; the iron is precipitated as sesquioxide, carrying with it a little cobalt, but the bulk of the cobalt remains dissolved, with any nickel which the ore may have contained.

The exact separation of cobalt from nickel is tedious. Two methods have been proposed, one by Rose, the other by Liebig (737). Rose's method is the following:—The two metals are thrown down from the ammoniacal liquid as sulphides, by the addition of ammoniac hydrosulphide. The sulphides are redissolved in nitric acid, the solution is then largely diluted, and acted upon by a current of chlorine; after this it is digested in a closed vessel for 12 hours upon powdered baric carbonate. The chlorine converts the cobalt into sesquioxide, which is gradually precipitated by the baric carbonate, and remains mixed with the excess of this carbonate employed. This precipitate is again dissolved in hydrochloric acid: the barium is removed by adding sodic sulphate, and the cobalt precipitated as protoxide by caustic soda: the precipitate must then be well washed with boiling water, and reduced in a current of hydrogen gas, which leaves the metal in the form of a black, highly magnetic powder. When

nickel is to be separated from cobalt for purposes of analysis, T. H. Henry recommends the substitution of a solution of bromine for chlorine gas in the foregoing process. Bromine may be used instead of chlorine in many analogous cases with great convenience.

If cobaltous oxide be reduced in a crucible lined with charcoal, a carbide of cobalt is formed, which may be obtained in a well-fused button. The crucible may be lined with charcoal for this purpose by dipping it into water, and filling it completely with charcoal finely powdered, and sufficiently moistened to render it coherent when firmly beaten into the crucible; a cylindrical cavity is then scooped out of the middle of the mass, and its interior is carefully smoothed with a glass rod, after which the crucible is allowed to dry slowly. Cobalt nearly pure may be procured by heating cobalt oxalate in a covered porcelain crucible, enclosed in a second earthen one, with the cover luted down; the crucibles are then exposed for an hour to the most intense heat of a forge: a well-fused button of cobalt may generally be obtained in this manner.

*Properties.*—Metallic cobalt is nearly as infusible as iron. It is of a reddish-grey colour, is hard, and strongly magnetic. Deville states that by reducing the oxalate in a crucible lined with lime, he obtained a metallic button which yielded a wire of a tenacity nearly double that of an iron wire of the same diameter. It is dissolved slowly, with evolution of hydrogen, by hydrochloric and diluted sulphuric acids, and it is freely attacked by nitric acid; when exposed to the atmosphere, it becomes slowly converted into oxide. Cobalt is not used in the metallic state in the arts. Many of the compounds of cobalt are remarkable for the beauty and brilliancy of their colour, and are used as pigments.

The alloys of cobalt are unimportant. Its compounds with arsenic are interesting, as they supply the greater part of the cobalt employed in the arts. *Tin-white cobalt* ( $\text{CoAs}_2$ ), when pure, contains 28.57 per cent. of cobalt and 71.43 of arsenicum; but portions of the cobalt are frequently displaced by nickel and iron. The purest specimens of this mineral are obtained from Tunaberg; the ore from this locality is the best material to employ in preparing the compounds of cobalt. Arsenide of cobalt melts at a moderate red heat. *Bright white cobalt*, or *cobalt glance* ( $\text{CoSAs}$ ), corresponds in composition to mispickel: it crystallizes in cubes, octohedra, or dodecahedra, and contains 35.54 per cent. of cobalt, 45.18 of arsenicum, and 19.28 of



sulphur. These minerals are violently decomposed by nitric acid or by aqua regia, and are readily attacked when heated in a current of gaseous chlorine. They are also decomposed when roasted in a current of air.

(720) OXIDES OF COBALT.—There are two well-marked oxides of cobalt, the protoxide, or cobaltous oxide,  $\text{CoO}$ , which is the salifiable base of the metal, and the sesquioxide,  $\text{Co}_2\text{O}_3$ ; these two oxides are capable of uniting with each other in different proportions. According to Schwarzenberg, an acid oxide,  $\text{Co}_3\text{O}_6$ , may be obtained in combination, by strongly igniting the protoxide or the carbonate with potassic hydrate, in which case a crystalline compound is formed, which when dried at  $100^\circ \text{C}$ ., consists of  $\text{K}_2\text{O}_3\text{Co}_3\text{O}_6 \cdot 3\text{H}_2\text{O}$ .

*Cobaltous oxide, or Protoxide of cobalt*; ( $\text{CoO} = 75$ ).—This oxide, when dried at a low temperature, is of a greenish-grey colour; when heated to dull redness in the air it absorbs oxygen, and becomes black, forming an oxide ( $\text{Co}_3\text{O}_4$ ) corresponding to the black or magnetic oxide of iron, but if more strongly heated it again loses oxygen, and becomes reconverted into the protoxide, which is of a brown colour, and which may be cooled in a current of carbonic anhydride without absorbing oxygen (Russell). Cobaltous oxide is soluble in acids, and forms solutions which, when concentrated, are of a beautiful blue colour, but they become pink on dilution. The oxide forms an important article of commerce, from its employment for the production of a blue colour in painting on porcelain. When describing the preparation of nickel, a process will be detailed which furnishes the oxide of cobalt fit for this purpose (729). Cobaltous oxide combines with bases as well as with acids. If fused with potassic hydrate it forms a blue compound, which is decomposed by the free addition of water; when heated with magnesian nitrate, a pale pink residue, formed by the combination of the magnesia with oxide of cobalt, is obtained; with alumina it forms the blue pigment known as Thénard's blue, and with zincic oxide the compound constitutes Rinman's green.

The *zaffre* of commerce is a very impure oxide of cobalt, procured by imperfectly roasting cobalt ore, mingled with 2 or 3 times its weight of siliceous sand.

*Smalt* is a beautiful blue glass coloured by oxide of cobalt; it is chiefly manufactured in Saxony. It is used largely by paper-stainers to produce a blue colour, and it is employed to some extent by laundresses for correcting the yellow tinge in linen. In preparing smalt, the cobalt ore is first roasted; but the roast-

ing is arrested at a particular stage, the object being to oxidize the cobalt, whilst the nickel, copper, and iron remain in combination with arsenic and sulphur; it is necessary to leave a sufficient amount of arsenic in the mass to retain these metals, as the admixture of a very small quantity of the oxides either of iron, nickel, or copper with the glass, seriously injures the purity of its colour.

From 4 to 5 parts of the roasted ore in powder are next mingled with 10 parts of ground calcined quartz and 4 parts of potassic carbonate, and the mixture is slowly melted in pots arranged in a furnace resembling that used in making ordinary glass. The oxide of cobalt combines with the fused potassic silicate; a deep blue glass is thus formed, whilst the mixed arsenides and sulphides of nickel, copper, and iron fuse, and collect at the bottom of the pot, in the form of a brittle mass, of metallic appearance, commonly known as *speiss*. The pot is then skimmed, and the glass is ladled out, and poured into cold water, by which means it is split into innumerable fragments: the *speiss* is cast into ingots and used in the manufacture of nickel. The broken glass is stamped to powder, and subsequently ground between granite stones, which are caused to revolve under water, in a vessel through which a gentle stream of water is continually flowing. The water as it flows carries off with it the powdered smalt in suspension: it is made to pass through a number of depositing vessels, so arranged that the overflow from the first shall pass into the second, that from the second into the third, and so on: each of these vessels is successively larger than the one which precedes it, so that the period for which the washings are retained in each goes on progressively increasing, and the particles deposited increase progressively in the minuteness of their subdivision; the colour becoming less intense, the greater the degree of subdivision of its particles.

Another valuable pigment into the composition of which cobalt enters is of a pale blue colour, and is known as *Thénard's blue*. The most approved method of preparing it consists of precipitating cobaltous nitrate by means of hydrodipotassic phosphate, and mixing the precipitate whilst still moist with four or five times its bulk of the gelatinous mass obtained by adding sodic carbonate to a dilute solution of alum perfectly free from iron. The mixture is dried and then exposed to a dull red heat in a covered crucible. The brilliancy of the colour is much impaired by the reducing action of the combustible gases of the fuel. The best preventive of this effect is found to consist in placing a little mercuric oxide at the bottom of each crucible; by the decomposition of this oxide an atmosphere of oxygen is obtained, and the metallic mercury is dissipated in vapour (Regnault, *Cours Élém. de Chimie*, vol. iii. p. 150).

*Rinman's green* is a pigment of analogous composition, containing oxide of cobalt combined with zinc oxide.

Hydrated cobaltous oxide ( $\text{CoO}, \text{H}_2\text{O}$ ) is precipitated by the addition of solution of potash or of soda to solutions of any of its salts. The pale blue precipitate which is first formed is a basic cobalt salt, but if an excess of alkali be used, it quickly becomes violet, and finally rose-coloured, which is the true colour of the hydrated oxide: these changes occur most rapidly if the liquid be warmed. It becomes of a dingy green if exposed while moist to the air, owing to the gradual absorption of oxygen. The hydrated protoxide is readily dissolved by a solution of ammoniac sesqui-

carbonate, and also by excess of ammonia, especially in the presence of a neutral ammonium salt.

*Cobaltic oxide*, or *Sesquioxide of cobalt* ( $\text{Co}_2\text{O}_3 = 166$ ) may be prepared by suspending the hydrated protoxide of the metal in water, and transmitting a current of chlorine through the liquid; cobaltous chloride is formed and dissolved, whilst a black hydrated cobaltic oxide is precipitated,  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . The reaction may be thus expressed:  $3(\text{CoO}, \text{H}_2\text{O}) + \text{Cl}_2 = \text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + \text{CoCl}_2$ . If the cobaltous oxide be suspended in a solution of potash instead of in pure water, the whole of the cobalt is converted into sesquioxide. It may be rendered anhydrous by a careful application of heat, but if strongly heated it becomes converted into a black oxide ( $\text{CoO}, \text{Co}_2\text{O}_3$ ), corresponding with the magnetic oxide of iron. This magnetic oxide is sometimes deposited in small, hard, anhydrous, brilliant, steel-grey octohedra when a pure aqueous solution of roseocobaltic chloride (721) is boiled. In this form it is insoluble in nitric acid, in hydrochloric acid, and in aqua regia: it is but slowly attacked by heating it with oil of vitriol or with hydropotassic sulphate. The basic powers of the sesquioxide are extremely feeble. Cold sulphuric, nitric, hydrochloric, phosphoric, and acetic acids dissolve the hydrated oxide, but the salts are gradually converted at ordinary temperatures into those of the protoxide, and this change is immediately effected if the solutions are heated.

(721) AMMONIACAL COMPOUNDS OF COBALT.—When a solution of a cobaltous salt in ammonia is exposed to the air, it absorbs oxygen rapidly, although the hydrated cobaltous oxide alone exhibits this tendency to a small extent only. If the hydrated oxide be dissolved in a solution of ammonic chloride containing free ammonia, the absorption of oxygen proceeds quickly, and a remarkable violet-red colour gradually develops itself in the liquid. If at this stage the liquid be supersaturated with hydrochloric acid in the cold, a heavy brick-red crystalline powder is precipitated, the *roseocobaltic* chloride ( $\text{CoCl}_2 \cdot 5\text{H}_2\text{N}, \text{H}_2\text{O}$ ; Genth and Gibbs); and this compound, if boiled, is converted into a purple precipitate of *purpureocobaltic* chloride ( $\text{CoCl}_2 \cdot 5\text{H}_2\text{N}$ ; Genth and Gibbs), which separates in crystals, leaving the solution nearly colourless: this precipitate may be dissolved by heating it in water slightly acidulated with hydrochloric acid, and as the liquid cools, beautiful ruby-red octohedral crystals are formed (F. Claudet). This remarkable compound is quite insoluble in boiling hydrochloric acid, and may be employed as a means of obtaining chemically pure cobalt: at a red heat it loses ammonia and ammoniac chloride, leaving cobaltous chloride. The latter may be reduced to the metallic state by passing a current of hydrogen gas over it in a tube heated to redness. When digested with water upon argentic oxide, the chlorine is withdrawn from the new compound, whilst the oxygen of the oxide takes its place; a red strongly alkaline liquid, purpureocobaltic oxide, is thus produced, which unites with acids, and forms a peculiar class of salts: this alkaline solution emits no smell of ammonia.

Fremy, in an elaborate series of researches on the ammoniacal compounds of cobalt, has shown (*Ann. de Chimie*, III. xxxv. 257) that, independently of the ammoniacal compounds obtained with the ordinary salts of the metal, and of the compounds above described, three other sets of salts may be procured, which he regards as compounds of different oxides of cobalt with various proportions of ammonia: the first of these bases he names *orycobaltia*. Its salts crystallize readily; they have for the most part an olive colour, and may be dissolved in a solution of ammonia without change, but when placed in cold water they are decomposed with evolution of oxygen and deposition of a green basic salt: the salts of this base appear to contain a dioxide of cobalt, which, however, cannot be isolated. The second base, from the yellow colour of its salts, he

erms *luteocobaltia*; this base has been isolated; it has a strongly alkaline reaction, and its salts crystallize easily. The third base is termed *fuscobaltia*; it forms brown uncrystallizable salts. The base of Claudet's salts, which Fremy termed, from the red colour of its compounds, *roseocobaltia*, is, according to Gibbs and Genth, a mixture of two isomeric bases, one of which, *roseocobaltia*, neutralizes 3 atoms of a monobasic acid; the other, *purpureocobaltia*, neutralizes only 2 atoms of acid. Further details regarding the preparation of these different compounds are also contained in a paper by Gibbs and Genth (*Chem. Gaz.* 1857, p. 141), who have described an additional series, to which they give the name of salts of *xanthocobalt*, from the brilliant yellow colour of these compounds. The xanthocobaltic chloride ( $\text{Co}_2\text{OCl}_2, 10\text{H}_2\text{N}, 2\text{NO}, \text{H}_2\text{O}$ ) may be obtained in crystals by decomposing the sulphate of this base with a solution of baric chloride; and the sulphate ( $\text{Co}_2\text{O}_4, 10\text{H}_2\text{N}, 2\text{NO}, 2\text{SO}_4, \text{H}_2\text{O}$ ) is easily procured by transmitting a rapid current of nitrous acid through an ammoniacal solution of cobaltous sulphate, taking care to preserve the alkalinity of the liquid by the occasional addition of ammonia. The solution gradually assumes a dark yellowish-brown colour, and if left to evaporate, spontaneously deposits the sulphate of the new base in the form of thin plates, derived from the right rhombic prism.

All the compounds of each of these bases, when boiled with a solution of caustic potash or of soda, are decomposed, and hydrated cobaltic oxide is precipitated, whilst ammonia is expelled.

The following table will afford a general comparative view of these different classes of salts, including the double salts which ammonia forms with the protoxide of the metal; they are probably compounds, of very complex constitution, formed on the ammonium type:—

1. *Double Salts of Ammonia and Protoxide of Cobalt.*

Nitrate	...	$\text{Co}_2\text{NO}_3, 6\text{H}_2\text{N}, 2\text{H}_2\text{O}$
Chloride	...	$\text{CoCl}_2, 6\text{H}_2\text{N}, 3\text{H}_2\text{O}$ .

2. *Salts of Oxycobaltia.*

Nitrate	...	$(\text{CoO}, \text{N}_2\text{O}_5)_5\text{H}_2\text{N}, \text{H}_2\text{O}$
Sulphate	...	$2[(\text{CoO}_2, \text{SO}_4)_5\text{H}_2\text{N}], 3\text{H}_2\text{O}$ .

3. *Salts of Luteocobaltia.*

Nitrate	...	$\text{Co}_3\text{NO}_3, 6\text{H}_2\text{N}$
Chloride	...	$\text{CoCl}_2, 6\text{H}_2\text{N}$ .

4. *Salts of Fuscobaltia.*

Nitrate	...	$\text{Co}_2\text{O}_4, 2\text{N}_2\text{O}_5, 8\text{H}_2\text{N}, 3\text{H}_2\text{O}$
Chloride	...	$\text{Co}_2\text{Cl}_2\text{O}_4, 8\text{H}_2\text{N}, 3\text{H}_2\text{O}$ .

5. *Salts of Xanthocobaltia.*

Nitrate	...	$\text{Co}_2\text{O}_4, 2\text{N}_2\text{O}_5, 10\text{H}_2\text{N}, 2\text{NO}, \text{H}_2\text{O}$
Chloride	...	$\text{Co}_2\text{OCl}_2, 10\text{H}_2\text{N}, 2\text{NO}, \text{H}_2\text{O}$ .

6. *Salts of Roseocobaltia (Gibbs and Genth).*

Nitrate	...	$\text{Co}_2\text{NO}_3, 10\text{H}_2\text{N}, 2\text{H}_2\text{O}$
Chloride	...	$\text{Co}_2\text{Cl}_2, 10\text{H}_2\text{N}, 2\text{H}_2\text{O}$ .

7. *Salts of Purpureocobaltia.*

Acid-sulphate	...	$\text{Co}_2\text{O}_4, 4\text{SO}_4, 10\text{H}_2\text{N}, 5\text{H}_2\text{O}$
Chloride	...	$\text{Co}_2\text{Cl}_2, 10\text{H}_2\text{N}$ .

(722) **SULPHIDES OF COBALT.**—Three sulphides of this metal may be procured,—a protosulphide,  $\text{CoS}$ ; a sesquisulphide,  $\text{Co}_2\text{S}_3$ ; and a disulphide,  $\text{CoS}_2$ . The latter may be obtained by heating cobaltous carbonate with sulphur, not allowing the temperature to rise too high. The most important of these is the *protosulphide*, which may be procured in a hydrated condition by precipitating a solution of cobaltous acetate by sulphuretted hydrogen, or by mixing any neutral solution of a cobalt salt with ammoniac hydrosulphide. In this form it speedily absorbs oxygen from the air, and becomes converted into cobaltous sulphate. If a mixture of cobaltous oxide with potassic persulphide (the liver of sulphur) be fused in a covered crucible, fused sulphide of cobalt is obtained at the bottom of the crucible. The *sesquisulphide*, which is occasionally met with in octahedra of a grey colour, may be obtained by heating cobaltic oxide to about  $500^\circ$  ( $260^\circ$  C.), in a current of sulphuretted hydrogen.

(723) *Cobaltous chloride, or Chloride of cobalt* ( $\text{CoCl}_2 = 130$ ; *Sp. Gr.* 2.937) is obtained as a lilac-coloured anhydrous mass, by passing chlorine over metallic cobalt; it is volatile at a high temperature. By dissolving cobaltous oxide or carbonate in hydrochloric acid, the hydrated chloride may be obtained in ruby-red octohedral crystals with  $6\text{H}_2\text{O}$  of *sp. gr.* 1.84, which are readily soluble in water and in alcohol; its aqueous solution when concentrated, or when mixed with an excess of strong hydrochloric acid, is of a deep blue colour, but on dilution it becomes pink. This dilute solution may be used as a sympathetic ink; characters traced with it on paper, though invisible when cold, become blue by heat, and again fade as the hygroscopic moisture of the paper is restored from the air: the colours of this ink may be varied at pleasure; the addition of a small proportion of a ferric salt renders it green; a salt of zinc produces a red, and one of copper a yellow tint. Anhydrous cobaltous chloride absorbs 4 atoms of ammonia, and if its solution be mixed with an excess of ammonia it deposits crystals, consisting of  $\text{CoCl}_2 \cdot 3[(\text{H}_4\text{N})_2\text{O}]$ .

(724) **COBALTOUS SULPHATE, or Sulphate of cobalt** ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O} = 155 + 126$ ; *Sp. Gr. anhydrous* 3.531) is isomorphous with magnesian sulphate. The anhydrous contains 38.06 of metallic cobalt, or 48.38 of the protoxide.

**COBALTOUS NITRATE, or Nitrate of cobalt** ( $\text{Co}_2\text{NO}_3 \cdot 6\text{H}_2\text{O} = 183 + 108$ ; *Sp. Gr.* 1.83), is prepared by dissolving the oxide in nitric acid. It is a deliquescent salt, which is sometimes employed as a reagent for the blowpipe: a fragment of the compound under examination is supported either upon charcoal, or

upon a bent platinum wire, and moistened with a minute quantity of a strong solution of the cobaltous nitrate. When treated in this way, many of the compounds of cobalt yield a pale pink-coloured mass after ignition; those of zinc give a green residue, and those of aluminum a blue.

If a concentrated solution of potassic nitrite be gradually added to a solution of cobaltous nitrate acidulated with nitric or with acetic acid, a beautiful orange-yellow compound is precipitated in microscopic four-sided prisms with pyramidal summits: it is sparingly soluble. According to A. Stromeyer, it consists of  $[\text{Co}_2\text{O}_3, 2\text{N}_2\text{O}_3, 6\text{KNO}_3, 2\text{H}_2\text{O}]$ , and contains 13.6 of metallic cobalt. Minute quantities of cobalt in admixture with nickel may be discovered by its means.

A hydrated *tricobaltous arseniate* ( $\text{Co}_3, 2\text{AsO}_4, 8\text{H}_2\text{O}$ ), is found native, in minute crystals, and is known as *cobalt bloom*.

(725) COBALTOUS CARBONATES.—Cobalt resembles magnesium, zinc, nickel, and copper, in the circumstance that when solutions of its normal salts are mixed with a solution of sodic or potassic carbonate, the precipitate which falls is not a normal carbonate, but a mixture of normal carbonate with hydrated cobaltous oxide. If the two solutions be mixed when hot, the red precipitate is said to have the formula  $(5\text{CoO}, 2\text{CO}_2, 4\text{H}_2\text{O})$ . If the salts be mixed at the ordinary temperature, the precipitate is of a brighter red, and has a composition  $(4\text{CoO}, 2\text{CO}_2, 7\text{H}_2\text{O})$ . If either of these precipitates be boiled with an excess of sodic carbonate, it assumes an indigo-blue colour, and is converted into the compound  $4\text{CoO}, \text{CO}_2, 4\text{H}_2\text{O}$ , which absorbs oxygen and becomes green during washing.

A true normal carbonate  $[3\text{CoO}, \text{CO}_2, 4\text{H}_2\text{O}]$  is formed by digesting either of the basic cobalt carbonates with the so-called bicarbonate of sodium or ammonia.

(726) CHARACTERS OF THE SALTS OF COBALT.—The crystallized cobaltous salts are red; when anhydrous they are usually lilac-coloured. Their solutions when in a very concentrated form are blue; at a particular stage of dilution they are red when cold, but become blue on heating them, the red colour returning as the liquid cools: when mixed with a larger proportion of water they exhibit a delicate rose colour, and this tint is perceptible even when the solution is very much diluted. They have an astringent metallic taste.

Before the blowpipe the compounds of cobalt are easily recognized by the intense blue colour which they communicate to a bead of borax in the oxidating flame.

In solution the salts which this metal forms with the mineral acids give no precipitate with *sulphuretted hydrogen*, if the liquid be slightly acidulated with sulphuric or hydrochloric acid; but the cobalt is completely precipitated by it from a dilute neutral solution of the acetate. With *hydro-ammonic sulphide* they yield a black sulphide. *Potassic carbonate* gives a rose-coloured basic carbonate, which is soluble in ammoniac sesquicarbonate. *Causitic potash* precipitates a blue basic salt, which by excess of the alkali becomes rose-coloured. *Ammonia* produces a similar effect, but readily dissolves the precipitate, forming a brownish solution which absorbs oxygen rapidly from the air and becomes red. The soluble *oxalates* give a sparingly soluble pink cobaltous oxalate, soluble in nitric acid and in ammonia. *Potassic ferrocyanide* gives a dirty green, and *potassic ferricyanide* a bulky reddish-brown precipitate; the latter reaction occurring even in ammoniacal solutions.

(727) *Estimation of Cobalt.*—Cobalt is often estimated in the metallic form. Supposing that no compound of any other metal susceptible of precipitation by sulphuretted hydrogen be present, the solution is to be neutralized by means of potassic carbonate, mixed with a solution of potassic acetate, and the cobalt precipitated as sulphide by a current of sulphuretted hydrogen, the precipitate allowed to settle in a beaker closed by a glass plate, then collected on a filter and washed. The alkalis are prevented from effecting the complete precipitation of cobalt, as well as of iron, nickel, copper, and many other metals, by the presence of certain kinds of organic matter, such as that derived from the paper of the filter; special precautions are therefore required to avoid this accident. For this purpose the neck of the funnel and the filter with its contents is introduced into a small flask, a hole is made with a glass rod in the bottom of the filter, and the precipitate is washed into the flask; the filter after being moistened with concentrated nitric acid, is again washed; it is then dried, burnt, and the ash added to the contents of the flask, which are now boiled with nitric acid until the cobaltous sulphide is dissolved. The liquid so obtained is diluted and poured off from any particles of undissolved sulphur, and the solution of cobalt may be evaporated to dryness, then mixed with sulphuric acid to convert it into sulphate, and the excess of acid expelled by a moderate heat. 100 parts of cobaltous sulphate indicate 38.06 of the metal. After the sulphide has been brought into solution by the nitric acid, the cobalt may also be precipitated in the form of hydrated oxide by an excess of

pure potash; the oxide is then thoroughly washed with boiling water, dried, ignited, and weighed: the black oxide thus procured consists of  $\text{Co}_3\text{O}_4$ , and corresponds to 72.44 of metallic cobalt. Some chemists, however, prefer to reduce this oxide by heating it in a weighed tube, in a current of dry and pure hydrogen; but the process is not to be recommended, as, if after the operation the tube be weighed full of hydrogen, the weight is too little, and if the hydrogen be displaced by atmospheric air, the finely divided reduced metal is apt to become partially oxidized.

3) *Separation of Cobalt from the Metals of the Alkalies and the Alkaline Earths, and from Aluminum.*—This is readily effected by converting the cobalt into acetate, and transmitting sulphuretted hydrogen, as has been already mentioned in the preceding paragraph. Another plan consists in the addition of ammoniac hydrosulphide to the solution previously neutralized by ammonia. If alumina be present, it will accompany the cobalt, but if this precipitate be redissolved in acid, and then thrown down by means of caustic potash in excess, the alumina will be retained; the cobaltous oxide is, however, apt to carry down traces of alumina; these may be removed by treating the precipitated oxide with means of a mixture of ammonia and ammoniac chloride, which dissolves the cobalt, but leaves only traces of alumina which may have accompanied it. The cobalt is again precipitated by ammoniac hydrosulphide.

*The separation of cobalt from zinc* is not easy. One of the best methods consists in precipitating the two metals together in the form of sulphides, dissolving this precipitate in nitric acid, and then adding an excess of potassic carbonate and evaporating to dryness. After the mixed carbonate of zinc and cobalt have been well washed, they are heated in a tube in a current of dried hydrochloric acid: in this process the carbonic acid is expelled, and the metals are converted into chlorides, whilst water is formed. The open end of the tube is in this case bent downwards at a right angle, and the aperture is made to dip into a small quantity of water contained in a flask: the zincic chloride, which is volatile, is carried forward in the current of gas; a portion of it is condensed in the bend of the tube, and the remainder is dissolved in the water placed for its reception. Cobaltic chloride alone remains in the bulb. The portion of the tube in which the zincic chloride has been condensed is cut off when the operation is complete, and is allowed to fall into the flask. The zinc and the cobalt are then easily determined separately by the usual methods.



§ H. NICKEL: (Ni''=59). *Sp. Gr.* 8.82.

(729) NICKEL is a metal the peculiar characters of which were first recognized in 1751 by Cronstedt: it has a remarkable analogy with cobalt, and always occurs associated with it in nature, both as a constituent of native iron, and in its ores, which present a composition similar to those of cobalt. It is most abundant in the form of kupfernickel (arsenide of nickel), and is extracted either from this ore or from *speiss*, which is an impure arseniosulphide of nickel, formed during the manufacture of salt (720).

*Preparation.*—As the metal itself is now extensively used in alloys, of which German silver is one of the most important, great pains have been taken to procure it in a state of comparative purity, and several processes have been proposed.

1.—According to Louyet, the method by which nickel is extracted from *speiss* at Birmingham on the large scale is as follows:—The *speiss* is first fused with chalk and fluor-spar, the metalliferous mass so obtained is reduced to powder, and roasted for two hours to expel the arsenic; the residue is next dissolved in hydrochloric acid; the solution is diluted, and the iron converted into a ferric salt by the cautious addition of bleaching powder. Milk of lime is then carefully added so long as ferric oxide falls, which carries down with it the last portions of arsenic; this precipitate is well washed, and the liquid, which retains all the cobalt and nickel, is treated with a current of sulphuretted hydrogen; the sulphides of copper, bismuth, and lead, are thus precipitated, and are thoroughly washed. All the nickel and cobalt still remains in the liquid; this liquid is boiled to expel sulphuretted hydrogen, neutralized with lime, and is again treated with chloride of lime: the whole of the cobalt is thus thrown down as sesquioxide: after which the whole of the nickel is separated from the solution in the form of hydrated protoxide by adding milk of lime so long as any precipitate is produced.

2.—Nickel may be obtained pure upon a small scale, by dissolving the roasted ore in aqua regia, evaporating to expel the excess of acid, redissolving in water, and transmitting a current of sulphuretted hydrogen. The filtered liquid is boiled with nitric acid, to convert the iron into a ferric salt; the solution is precipitated by an excess of caustic ammonia, filtered from the ferric oxide, and to the blue liquid caustic potash is added until the blue tint nearly disappears; a pale green precipitate, consisting of hydrated nickel oxide and potash, is thus obtained, which must be well washed with hot water to remove the potash, and then reduced by ignition in a current of hydrogen gas: when obtained in this manner it is generally pyrophoric. If heated for an hour by means of a blacksmith's forge, in a crucible lined with charcoal, a well-fused button of carbide of

nickel is produced. A button of the pure metal may however be procured by heating nickel oxalate intensely in a crucible with a luted cover, without any other reducing agent than the carbonic oxide furnished by its own decomposition.

3.—It may also be obtained in laminae by the electrolysis of a solution of the ammonio-nickel sulphate ( $\text{NiSO}_4 \cdot (\text{H}_4\text{N})_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ).

*Properties.*—Pure nickel is a brilliant, silver-white, hard, but ductile metal, little more fusible than iron; which, according to Deville, it even surpasses in tenacity. At ordinary temperatures it is susceptible of magnetism, but it loses this property almost entirely if heated to a point exceeding  $626^\circ$  ( $330^\circ$  C.), though it recovers its magnetic power on cooling. Nickel becomes oxidized by exposure to a current of air at a high temperature. The metal is easily attacked at ordinary temperatures by chlorine or bromine if suspended in water. It is also readily dissolved by nitric acid and by aqua regia, and is dissolved slowly with evolution of hydrogen by diluted sulphuric or by hydrochloric acid. Owing to the remarkable whitening power which nickel exerts on brass, it is now much used in the manufacture of *packfong*, or German silver, a compound of zinc, nickel, and copper, in which the proportions of the metals may vary considerably. A good alloy consists of 5 equivalents of copper, 3 of zinc, and 2 of nickel, or, in 100 parts, of 51 of copper, 30.6 of zinc, and 18.4 of nickel. Packfong is of a yellowish-white colour, and when freshly polished closely resembles silver in appearance. *Tutenag* is the name given by the Chinese to a similar alloy, consisting of 8 parts of copper,  $6\frac{1}{2}$  of zinc, and  $\frac{2}{3}$  of nickel.

The native arsenides of nickel are important, as they form the principal ores of the metal. *Kupfernickel* ( $\text{NiAs}$ ) is true nickel arsenide; it contains 44 parts of nickel to 56 of arsenicum; part of the arsenicum in this ore is sometimes displaced by an equivalent amount of antimony. It has a reddish colour and a metallic lustre. It is not attacked by hydrochloric acid, but is soluble in nitric acid, and is decomposed when heated in air or in a current of chlorine. *Arsenical nickel* ( $\text{NiAs}$ ) is another native compound of the two metals: by ignition in closed vessels it loses half its arsenicum, and becomes converted into kupfernickel. A compound of nickel with arsenicum and sulphur, corresponding to mispickel, and known as *nickel glance* ( $\text{NiSAs}$ ), is also found native.

(730) OXIDES OF NICKEL.—Nickel forms two oxides; a protoxide,  $\text{NiO}$ , and sesquioxide,  $\text{Ni}_2\text{O}_3$ . The first only forms salts.

*Nickelous oxide*, or *Protoxide of nickel* ( $\text{NiO}=75$ ); *Sp. Gr.* 5.75; *Comp. in 100 parts*, Ni, 78.67; O, 21.33.—This oxide may be obtained in the anhydrous form by igniting the nitrate or the

carbonate of the metal in a covered crucible, when it is left of an olive-green colour. It may be precipitated from its salts by potassic hydrate, as a bulky light-green hydrate ( $\text{NiO}, \text{H}_2\text{O}?$ ), and may be obtained crystallized by decomposing the solution of nickel carbonate in ammonia by ebullition. Nickelous oxide is readily soluble in acids, forming salts which have a pale green colour. It yields insoluble compounds with potash and with soda, which, however, may be decomposed by frequent washings with boiling water. Baryta, strontia, and several other bases also form with it insoluble compounds; ammonia dissolves it, forming a deep blue solution. A solution of ammoniac chloride also dissolves it slowly.

The sesquioxide ( $\text{Ni}_2\text{O}_3 = 166$ ) is a black powder which may be procured as a hydrate with  $3\text{H}_2\text{O}$ , by treating the hydrated protoxide with a solution of chloride of soda. It does not combine with acids, and gives off a portion of its oxygen by ignition, or by heating it with nitric or sulphuric acids, which form with it salts of the protoxide.

(731) SULPHIDES OF NICKEL.—Three of these compounds are known; a subsulphide, a protosulphide, and a disulphide. The *protosulphide* ( $\text{NiS} = 91$ ) occurs native as *millerite* in greyish or yellowish capillary crystals, which are insoluble in hydrochloric, but soluble in nitric acid: it may be formed artificially by fusion of sulphur with nickel. It may also be procured by fusing a persulphide of one of the alkali-metals with diarsenide of nickel, and is left in yellow crystalline scales. A black hydrate of this sulphide is produced when a salt of nickel is precipitated by ammoniac hydrosulphide; in this form it absorbs oxygen from the air, and is gradually converted into nickel sulphate. The *subsulphide* ( $\text{Ni}_3\text{S}_2$ ) may be formed by reduction of nickel sulphate by means of charcoal or of hydrogen gas. The *disulphide* ( $\text{NiS}_2$ ) is obtained as a steel-grey powder on treating with water the mass obtained by heating to redness an intimate mixture of nickel carbonate, potassic carbonate, and sulphur.

(732) NICKEL CHLORIDE, or *Chloride of nickel* ( $\text{NiCl}_2 = 130$ ), is formed by dissolving the oxide in hydrochloric acid. Its solution, on evaporation, yields green hydrated crystals with  $9\text{H}_2\text{O}$ ; by heat it may be obtained as a yellowish-brown anhydrous mass, which at a high temperature is volatile, and condenses in yellow crystalline scales, which are dissolved slowly by boiling water. If heated in a current of air, a portion of the chlorine is expelled, and a corresponding quantity of nickelous oxide is formed.

(733) NICKEL SULPHATE, or *Sulphate of nickel* ( $\text{NiSO}_4, 7\text{H}_2\text{O} = 155 + 126$ ).—This salt may be obtained by dissolving

metallic nickel, or its oxide or carbonate, in sulphuric acid. It crystallizes in green rhombic prisms, which require 3 parts of cold water for solution: the prismatic crystals, when exposed to light, are converted into small regular octohedra, aggregated together in the form of the original crystal, which becomes opaque. It may be obtained in octohedra at once with  $6\text{H}_2\text{O}$  (*sp. gr.* 2.037), by crystallizing at a temperature between  $59^\circ$  and  $77^\circ$  ( $15^\circ$  and  $25^\circ \text{C.}$ ).

A *potassio-nickel sulphate* ( $\text{NiSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ; *sp. gr. anhydrous*, 2.897, *cryst.* 2.190) may be formed by adding caustic potash to the impure solution of speiss, and by repeated crystallizations may be freed from all impurities except traces of iron and cobalt: it was at one time used as a means of purifying nickel for commercial purposes. Other double sulphates of nickel may be formed. Each atom of nickel sulphate in the solid form absorbs 6 atoms of ammoniacal gas. An insoluble *basic sulphate* is obtained by adding to a solution of the normal sulphate a quantity of potassic hydrate insufficient for its complete decomposition.

(734) **NICKEL CARBONATES.**—There are several basic nickel carbonates, of a green colour. The normal carbonate is precipitated as a crystalline powder, when a solution of nickel nitrate is poured into a large excess of a solution of hydrosodic carbonate (bicarbonate of soda).

(735) **CHARACTERS OF THE SALTS OF NICKEL.**—The salts of this metal are of a delicate green colour, both when in the solid state and when in solution; they redden blue litmus feebly. They have a sweetish astringent metallic taste, and when taken internally excite vomiting.

*Before the blowpipe*, the salts of nickel give in the oxidating flame with borax a reddish-yellow glass, which becomes much paler as it cools. The addition of a potassium salt colours the bead blue. In the reducing flame, greyish particles of reduced nickel are disseminated through the bead.

In solution, *sulphuretted hydrogen* gives no precipitate if the liquid be acidulated with sulphuric acid; but it precipitates a diluted solution of nickel acetate, if nearly neutral, very perfectly when aided by a gentle heat. *Hydro-ammonic sulphide* gives a black sulphide slightly soluble in excess of the precipitant, forming a dark-brown solution. *Ammonia* gives a pale green precipitate, soluble in excess of ammonia, forming a bright blue solution, from which an excess of potash precipitates a green compound of nickelous oxide and potash. *Potassic* and *sodic hydrates* throw down a pale-green bulky hydrated nickelous oxide, insoluble in excess of the alkali. The *carbonates of the alkali-metals* give a pale apple-green precipitate of basic nickel carbonate, which is readily soluble in ammonic sesquicarbonate. *Potassic ferrocyanide* gives a greenish white, and *potassic ferricyanide*

anide a yellowish-green precipitate, both of which are soluble in hydrochloric acid. *Hydro-potassic oxalate* in a neutral solution, if not too dilute, causes the deposition of a greenish-white sparingly soluble nickelo-potassic oxalate soluble in excess of ammonia.

(736) *Estimation of Nickel*.—Nickel is best estimated in the form of protoxide, which, when precipitated by means of caustic potash, requires patient washing with hot water to remove the adhering alkali: 100 parts of nickelous oxide contain 78.67 of the metal.

*Separation of Nickel from the Alkalies and Earths, and from Zinc*.—For this purpose the same processes as those adopted for the separation of cobalt (728) may be employed.

(737) *Separation from Cobalt*.—The following method, advised by Liebig and slightly modified by Hadow, is the best for this purpose. The nitric solution of the cobalt and nickel having been freed from all other metals except potassium or sodium, after being nearly neutralized with potassic carbonate, is mixed with an excess of hydrocyanic acid, and then with pure caustic potash, after which the mixture is left exposed to the air in a shallow open dish for a few hours. During this time oxygen is absorbed, and the liquid acquires a pale yellow colour. A tripotassic cobalticyanide ( $K_3CoCy_6$ ) is formed, and a nickelo-potassic cyanide ( $2KCy, NiCy_2$ ) is produced at the same time. The formation of the cobalticyanide may be traced as follows: cobaltous cyanide is first formed;  $2HCy + CoO = CoCy_2 + H_2O$ , and this cyanide, by exposure to air with an excess of potassic cyanide and hydrocyanic acid, yields tripotassic cobalticyanide, whilst oxygen is absorbed and water is separated;  $4CoCy_2 + 12KCy + 4HCy + O_2 = 4K_3CoCy_6 + 2H_2O$ . The nickelo-potassic cyanide is very simply formed; for with nickel no compound corresponding to the cobalticyanide is obtained;  $4KCy + NiO + H_2O = 2KCy, NiCy_2 + 2KHO$ . If the strongly alkaline solution be now boiled and a solution of mercuric nitrate be added in slight excess, so as to produce a precipitate which, from its yellowish colour, shows that the mercuric oxide is in excess, the nickel salt is decomposed, hydrated nickelous oxide is precipitated, and mercuric cyanide is produced;  $2KCy, NiCy_2 + HgO + H_2O = 2KCy, HgCy_2 + NiOH_2O$ .

Potassic cobalticyanide is not decomposed by mercuric oxide, but remains in solution, and may be filtered from the nickelous oxide, which requires to be carefully ignited in a platinum crucible till it ceases to lose weight. After cautiously neutralizing the filtrate with nitric acid, the cobalt may then, by the addition

of a solution of mercurous nitrate, be precipitated as a white mercurous cobalticyanide: the precipitate is collected, dried, and ignited in a porcelain crucible, when pure cobaltous oxide is left.

If, instead of precipitating the mixed cyanides by means of mercury, a solution of chloride of soda be added in excess to the boiling alkaline liquid, in quantity sufficient to destroy the free potassic cyanide, the nickel is precipitated of an intense black as sesquioxide; in this form it may be readily washed, and by ignition it may be converted into the protoxide, in which state it may be weighed. Traces of nickel which escape discovery by other methods may thus often be detected in cobalt. Care must be taken to ascertain the absence of manganese, as it would go down with the nickel, accompanied by traces of iron, if the latter metal were present.

### § III. URANIUM: ( $U=120$ ). *Sp. Gr.* 18.4.

(738) URANIUM is a metal the compounds of which are but sparingly distributed over the surface of the earth. It was originally discovered by Klaproth, in *pitchblende*, which contains nearly 80 per cent. of the black uranium oxide ( $2UO, U_2O_3$ ); the remainder of the mass consists of variable quantities of copper, lead, iron, arsenicum, and frequently of cobalt and nickel. *Uranite*, which is a mineral of micaceous structure, of rarer occurrence, consists of a hydrated calcic diuranic diphosphate [ $Ca''2(U_2O_3)''2PO_4, 8H_2O$ ]. *Chalcolite* [ $Cu''2(U_2O_3)''2PO_4, 8H_2O$ ] is a similar mineral, in which copper takes the place of calcium.

In order to extract uranium from pitchblende, the mineral is heated to redness, and thrown whilst red-hot into water, after which it admits of being readily pulverized: Ebelmen then treats the ore in the following manner:—The fine powder is washed with diluted hydrochloric acid, heated with charcoal, and digested in strong hydrochloric acid, by which the earthy matters and most of the iron, arsenic, and sulphur are removed: the washed residue is roasted and then treated with nitric acid; the solution thus obtained is evaporated nearly to dryness, to expel the excess of acid, and is diluted, by which means most of the ferric arseniate is precipitated. Sulphuretted hydrogen is then transmitted through the filtered solution, and the liquid is filtered from the sulphides of copper, lead, and arsenic thus thrown down; after which it is again evaporated until crystals of uranic nitrate begin to be formed. This salt is decomposed by heating it to redness, and the uranium oxide which is left is mingled with charcoal and heated in a glass tube through which a current of dry chlorine is passing; carbonic anhydride and carbonic oxide are thus formed, and a volatile green uranous chloride ( $UCl_3$ ) sublimes. This chloride, when heated with potassium in a platinum crucible, yields potassic chloride and metallic uranium: intense heat is evolved during the reaction of the potassium on the uranous chloride, and the resulting metal is partially fused. The isolation of metallic uranium is due to Pélignot (*Ann. de Chimie*, III. v. 5), the substance originally supposed to be the metal having been proved by him to be its protoxide.

Uranium as thus obtained is of a steel-white colour : it appears to be slightly malleable ; it is not oxidized by exposure to air or to water at ordinary temperatures : but if heated in the air it burns brilliantly : sulphuric and hydrochloric acids dissolve it with extrication of hydrogen gas. In its chemical relations it is somewhat analogous to iron and manganese.

(739) URANIUM OXIDES.—Uranium forms two principal oxides, a *protoxide*, or *uranous oxide*,  $\text{UO}$ , and a *sesquioxide*, or *uranic oxide*,  $\text{U}_2\text{O}_3$  ; besides these a suboxide ( $\text{U}_4\text{O}_3$ ?) appears to exist : two intermediate oxides may also be obtained, the *black oxide*,  $2\text{UO}, \text{U}_2\text{O}_3$ , and the *green oxide*,  $\text{UO}, \text{U}_2\text{O}_3$ .

The *protoxide*, or *uranous oxide* ( $\text{UO} = 136$ ), may be obtained in several ways : one of the easiest consists in igniting uranic oxalate in closed vessels, or in a current of hydrogen. In its anhydrous state the dilute acids are without action upon it, but its hydrate, which may be obtained in reddish-brown flocculi, by adding ammonia to a solution of uranous chloride,  $\text{UCl}_2$ , is readily soluble in the acids ; it forms green crystallizable salts, which have a strong tendency to absorb oxygen.

The *black oxide* ( $2\text{UO}, \text{U}_2\text{O}_3$ ) may be procured by heating the protoxide to bright redness, and suddenly cooling it, or by igniting uranic nitrate. It furnishes a pure and intense black, highly prized for colouring porcelain.

The *green oxide* ( $\text{UO}, \text{U}_2\text{O}_3$  ; *sp. gr.* 7.31), which corresponds in composition to the magnetic oxide of iron, is procured by heating the black oxide moderately in a current of oxygen or in the open air ; by more intense ignition it becomes re-converted into the black oxide, and is again partially re-oxidized as it cools. It is soluble in hot concentrated sulphuric acid, but does not form distinct salts.

The *sesquioxide*, or *uranic oxide* ( $\text{U}_2\text{O}_3$ ), partakes of the character both of an acid and of a base. It is with difficulty obtained in a pure state. By exposing uranic oxalate to the sun's rays, a brownish-violet powder, which is a hydrate of the green oxide ( $\text{U}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ), is deposited, while carbonic anhydride makes its escape : this precipitate absorbs oxygen on exposure to the air, and becomes converted into a greenish-yellow mass, which, according to Ebelmen, is a hydrated sesquioxide ( $\text{U}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ). The sesquioxide may be obtained in the anhydrous state as a brick-red powder, by heating this hydrate to a temperature not exceeding  $572^\circ$  ( $300^\circ \text{C.}$ ) Uranic oxide reacts readily with acids, and forms salts of a bright yellow colour. Péligré found that the oxide ( $\text{UO}$ ) evinced a strong tendency to unite with elementary bodies

like a metal, and hence he proposed to call it *uranyl*, and he explained the fact that the normal uranic salts are all formed by the action of uranic oxide upon two atoms of a monobasic acid instead of on six atoms. Uranic nitrate, for instance, which furnishes long striated prisms, consists, even when crystallized from a strongly acid solution, of  $(U_3O_8) \cdot 2NO_3 \cdot 6H_2O$ . Numerous uranic double salts have also been formed; uranico-potassic sulphate consists of  $(K_2(U_3O_8) \cdot 2SO_4 \cdot 2H_2O)$ . If an attempt be made to procure uranic oxide by decomposing the solutions of these salts by the addition of an alkali, an insoluble yellow precipitate, consisting of a compound of the sesquioxide with the alkali, frequently called a *uranate* of the base, falls; potassic uranate has the formula,  $K_2O \cdot 2U_3O_8$ , and the other similar compounds have a corresponding composition; this compound cannot be decomposed even by boiling water: the commercial yellow oxide is a hydrate retaining about 2 per cent. of ammonia, from which heat expels the water and ammonia, and also converts the sesquioxide into the black or the green oxide. The compounds of uranic oxide with the earths, however, stand a strong heat without decomposition, and are employed to communicate a beautiful and peculiar yellow to glass.

(740) URANIUM CHLORIDES.—Uranium forms two chlorides, one  $(U_2Cl_6)$  corresponding to the suboxide, and another,  $UCl_4$ , corresponding to uranous oxide, besides an oxychloride ( $UOCl$ ). The *dichloride* ( $UCl_4$ ), *uranous chloride* (Péligot's protochloride) is a green, volatile, deliquescent compound, which is decomposed by water; the method of preparing it has already been described (738). If dry hydrogen gas be transmitted over uranous chloride, while it is being heated to redness in a glass tube, a *sesquichloride* ( $U_2Cl_6$ ) is produced; it crystallizes in slender dark-brown needles, which are but slightly volatile; they are very soluble in water, and form a deep purple solution, from which ammonia throws down a brown suboxide; this oxide absorbs oxygen from the air rapidly. An *oxychloride* ( $UOCl$ ), or  $(U_2O_5 \cdot UCl_3)$ , somewhat analogous to chlorochromic acid (789), is formed by passing chlorine over uranous oxide, constituting Péligot's *chloride of uranyl*: it is deliquescent, and forms a yellow solution with water; with the chlorides of the alkali-metals it yields remarkable double salts; the double salt with potassic chloride consists of  $(KCl, UOCl, H_2O)$ , and crystallizes in rhombic tables of a greenish-yellow colour.

(741) CHARACTERS OF THE URANIUM COMPOUNDS.—I. The *uranous salts* have a green colour, and have a strong tendency to form double salts with salts of the alkali-metals which contain the same acid as themselves. In solutions of the uranous salts, *ammonia* and the *alkalies* give a gelatinous, blackish-brown precipitate of hydrated uranous oxide: this precipitate absorbs oxygen and becomes yellow from the formation of uranic oxide, which unites with the excess of alkali. *Sulphuretted hydrogen* produces no precipitate; but *ammonic hydrosulphide* occasions a black



deposit of sulphide of uranium. *Ammonic oxalate* gives a greenish-white precipitate of uranous oxalate. Solutions of the green salts of uranium absorb oxygen rapidly, and are converted by nitric acid into uranic salts, even without the aid of heat.

2.—*The uranic salts* are yellow. Their solutions give with *ammonia* a yellow precipitate, consisting of ammonic uranate: with *potassic ferrocyanide* they yield a hair-brown precipitate. By the action of ammonia they are distinguished at once from the compounds of copper, which give a blue solution on the addition of an excess of ammonia, though they yield a precipitate with the ferrocyanide similar in colour to that furnished by the salts of uranium. *Sulphuretted hydrogen* produces no precipitate; but *ammonic hydrosulphide* gives a yellowish-brown sulphide. *Carbonates of the alkali-metals* give a yellow granular precipitate, soluble in excess of the precipitant; these precipitates are double carbonates of uranium and the alkali-metal employed. With *infusion of nut-galls* a dark-brown precipitate is produced.

(742) *Estimation of Uranium*.—Uranium is usually estimated in the form of protoxide, to which it is reduced by heating the sesquioxide to redness in a glass tube in a current of hydrogen; the tube must be sealed up whilst full of hydrogen, and weighed in this condition, to prevent the oxide from reabsorbing oxygen from the air.

Uranium is separated from the alkalies by converting it into a uranic salt by nitric acid, if not already in that condition, and then precipitating it in the form of yellow ammonic uranate. If barium, strontium, calcium, or magnesium be present, the addition of sulphuric acid separates the first two in the form of sulphates; if calcium or magnesium be present, the solution is filtered from the precipitate, the filtrate evaporated to dryness, and then heated with alcohol of specific gravity 0.900; the calcic and magnesic sulphates remain unacted upon, while the uranic sulphate is dissolved.

Aluminum, glucinum, zinc, cobalt, and nickel may be separated from uranium by adding hydrotassiac carbonate in excess to the acidulated solution: a uranico-potassic carbonate remains in the liquid, while the earths, and other metallic oxides, are precipitated. For the success of this experiment it is necessary, if salts of ammonium be present, that they should be expelled, by evaporating the solution to dryness and igniting the residue, before effecting the precipitation of the various bases with the hydrotassiac carbonate.

§ IV. IRON (Ferrum):  $\text{Fe}'' = 56$ ; *Sp. Gr.* 7.844; *Dyad in the ferrous Salts*, as  $\text{FeCl}_2$ ; *Triad in the ferric Salts*, as  $\text{Fe}_2\text{Cl}_6$ .

(743) *Condition of Iron in Nature*.—IRON is more extensively diffused than any other metal: not only is it abundant in the inorganic creation, but it is an essential constituent in the blood of the vertebrate animals.

Iron has been occasionally found in the native form accompanying the ores of platinum; but when it occurs in the metallic

state it is generally met with in meteoric masses associated with nickel, cobalt, and small quantities of other metals, among which are copper, manganese, and chromium. Some of these masses which have fallen in an ignited state from the atmosphere are of very considerable size. One discovered in Siberia, by Pallas, weighed 725 kilos., or 1600 lb., and a block found in the district of Chaco-Gualamba, in South America, is estimated at between 13 and 14 tons weight. These extraordinary bodies are unimportant as sources of iron.

Aërolites, or meteoric stones, may be subdivided into three principal groups, the first of which consists of metallic masses, and these are the most common: the second variety contains no metallic iron, but consists often of crystalline minerals; and the third not uncommon form is composed of a mixture of the metallic and earthy variety in the same specimen. These different kinds of aërolites are usually inclosed in a thin crust or rind of a millimetre or two in thickness, presenting a glossy, pitch-like, or veined surface. The crystalline minerals which have been observed are of a basaltic nature, and consist of olivine, varieties of augite and leucite, anorthite and labradorite; in addition to these, chrome iron, tinstone, magnetic iron ore, and magnetic pyrites have been found, besides nickeliferous metallic iron.

The masses of meteoric iron themselves also display a crystalline structure. When a polished surface of one of these metallic masses is immersed in nitric acid, the different portions of the surface are unequally acted upon, as was first noticed by Widmannstatt: and a series of lines crossing each other in three different directions become developed; between them are broad shallow spaces, less deeply etched, and narrow bands between these retain their polish and resist the acid; these bands contain more nickel than the rest of the mass.

The origin of these meteorites is unknown; but it is an opinion generally received, that they are asteroids or planetary dust, fragments of which from time to time come within the sphere of the earth's attraction: these, by friction in their rapid flight through the earth's atmosphere, become ignited, and ultimately reach the surface of the earth.

Amongst the constituents of these meteorites twenty-two elementary substances have been found, but no element not previously known to be of terrestrial origin has been discovered. The following are the meteoric elements, partly in the earthy, partly in the metallic portions:—

Iron.	Magnesium.	Arsenicum.
Cobalt.	Calcium.	Phosphorus.
Nickel.	Potassium.	Nitrogen.
Chromium.	Sodium.	Sulphur.
Manganese.	Aluminum.	Oxygen.
Copper.	Titanium.	Chlorine.
Tin.	Silicon.	Bromine.
	Carbon.	

The metallic portions consist chiefly of native iron, which contains sulphur, phosphorus, carbon, manganese, magnesium, nickel, cobalt, tin, and copper.

The ores of iron are numerous. The most valuable are the following:—

1.—*Magnetic iron ore*, or *Loadstone* ( $\text{FeO}, \text{Fe}_2\text{O}_3$ ); *Sp. Gr.* 5.09.—This is found in enormous masses, or even mountains,

amongst the primary formations. Much of the best Swedish iron is obtained from this material, which is also abundant in North America. Occasionally it is found in detached octohedral crystals. Coal is absent in those formations in which this mineral occurs; hence charcoal is the fuel ordinarily employed in smelting it. This fuel contains a smaller amount of ash than coal; fewer impurities are therefore introduced by it during the smelting than when coal is used; and as the ore itself is generally very pure, the metal which it furnishes is of excellent quality. The heavy lustrous black *iron sand* found at Nellore, in India, and employed in the manufacture of wootz, consists chiefly of magnetic oxide of iron.

2.—*Specular iron ore*, or *Fer oligiste*; *Sp. Gr.* 5.2.—This is an anhydrous sesquioxide of iron ( $\text{Fe}_2\text{O}_3$ ): it occurs in the primary rocks. The principal part of the celebrated Elba iron, and also a large quantity of Russian and of Swedish iron, are obtained from this source. Charcoal is in this case also the fuel employed.

3.—*Red hæmatite* ( $\text{Fe}_2\text{O}_3$ , *sp. gr.* about 5.0) is another form of the anhydrous sesquioxide; it is sometimes found massive; but more generally in fibrous crystalline nodules. This ore is largely raised near Whitehaven and in some parts of Cornwall. It is seldom smelted alone; but it forms a valuable addition to the clay iron-stone of the coal-measures.

4.—*Brown hæmatite* ( $2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}$ ); *Sp. Gr.* about 3.9.—This is a hydrated sesquioxide of iron, which generally occurs in fibrous or in compact masses. It is, however, also met with in the oölitic strata, in some parts of France, in the form of rounded masses, termed *pea-iron ore*, mixed with a small proportion of clay. Much of the French iron is obtained from this source. Brown hæmatite is readily soluble in hydrochloric acid; it is less refractory in the furnace than the preceding variety. The brown hæmatite, when roasted, becomes porous from the loss of its water, and is thus rendered more manageable. Mixed with variable proportions of earth or clay, and sometimes with oxide of manganese, this oxide of iron forms the varieties of umber and ochres. It occurs principally in the secondary and tertiary deposits.

5.—*Spathic iron*, or *Ferrous carbonate* ( $\text{FeCO}_3$ ); *Sp. Gr.* 3.8.—This is found in crystalline masses often combined with magnesian carbonate, and with a considerable proportion of manganese, as in the Saxony ores. Much of the so-called *natural steel* is made from this ore.

6.—*Clay ironstone* is the chief source of the enormous quantity of iron manufactured in Great Britain. It is an impure

ferrous carbonate, containing generally from 30 to 33 per cent. of metallic iron, mingled with varying proportions of clay, oxide of manganese, lime, and magnesia. This argillaceous ironstone occurs in bands broken up into nodules, or in continuous seams, from 5 to 35 centim. (2 to 14 inches) thick, alternating with beds of coal, clay, shale, or limestone, in the coal-measures, diffused over large areas in South Staffordshire, South Wales, and some other parts of Great Britain. It is also found in the United States, and in Bohemia and other countries of central Europe. It has a specific gravity ranging between 2·7 and 3·47.

7.—*The black-band* of the Scotch coal-fields is also a ferrous carbonate, but the principal foreign matter in this mineral, which often amounts to 25 or 30 per cent., is of a bituminous or combustible nature.

8.—A siliceous ironstone containing both ferric oxide and ferrous carbonate has been found abundantly in the oölite in the neighbourhood of Northampton. It yields an inferior iron, owing to the presence of a large quantity of phosphates in the ore.

9.—Another, but comparatively an unimportant ore, of a brown colour, known as *bog-iron ore*, is a mixture of hydrated ferric oxide and phosphate in variable proportions. It occurs in marshy alluvial districts, near the surface.

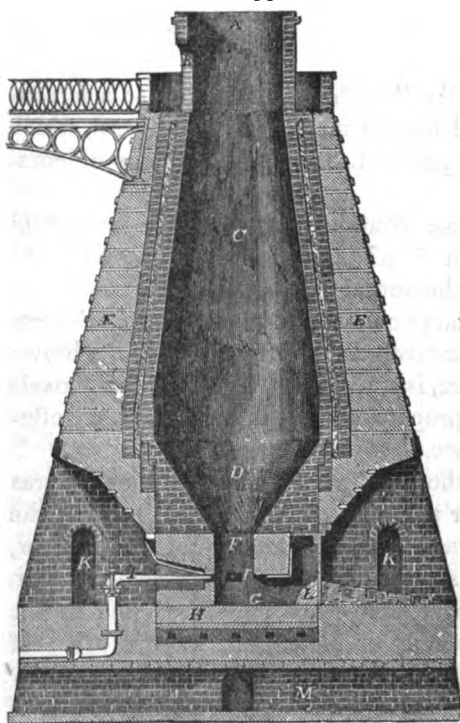
Iron pyrites ( $\text{FeS}_2$ ), though a very abundant mineral, was formerly wrought only for the sake of its sulphur, because the iron which it furnished was not pure enough for use. Now, however, by roasting the residue after burning, with common salt, the small quantity of copper and other metals, as well as the residual sulphur, are completely extracted, and a pure oxide of iron is obtained, largely used in lining puddling furnaces.

(744) SMELTING OF CLAY IRONSTONE.—After the ore has been broken up into masses about the size of two fists, it is generally roasted, in order to expel water and carbonic acid; the mass is thus left in a porous state, highly favourable to its subsequent reduction in the furnace. The roasting is sometimes performed in kilns, but usually in heaps in the open air. If this operation is to be effected in the open heap, a plat of ground is levelled and covered with a layer of coal in lumps to the depth of 25 or 30 centimetres (10 or 12 inches); this is succeeded by alternate layers of the mineral and of small coal. The quantity of coal required in the case of the black-band is often very small, as the ore itself frequently contains sufficient inflammable matter to continue burning when once well lighted. The heap, when finished,

is from 4.25 to 4.5 metres wide, 2.5 to 3 metres high (or about 14 or 15 feet wide and 8 or 10 high), and is of great length. The fire is kindled at the windward extremity, and allowed to spread gradually through the mass. This preliminary operation occupies some months for its completion. The roasted ore is then ready for the smelting.

The *blast furnace* employed for this purpose is represented in section in fig. 355. The

FIG. 355.



internal cavity in shape resembles a long narrow funnel inverted upon the mouth of another shorter funnel. These furnaces are usually about 15 metres or 50 feet high, and from 4.25 to 5 metres, or from about 14 to 17 feet, in diameter in the widest part of the cavity. The lowest portion, F, or neck of the funnel, is termed the *crucible* or *hearth*, and is made of very refractory gritstone. In the front, 20 or 25 centimetres (8 or 10 inches) from the floor, H, is a longitudinal aperture above the *tympan-stone*, L, for the overflow of the slag, and on the sides are the openings

for the *tuyères*, I, I, or blast-pipes, which are connected with powerful blowing machines for supplying air under a pressure of from 2 lb. to 3 lb. upon the inch. A steady and most intense heat is thus uniformly maintained. At the lowest point of the furnace is the *tap-hole*, for drawing off the melted metal at suitable intervals, and which, except at such times, is closed with sand and clay: K, K, are galleries, for allowing the workmen free access to the tuyères and lower portion of the furnace, the base of which is kept dry and well drained by the arched channels, M. Above the crucible the furnace suddenly widens, forming the *boshes*, D; the lining, C, is formed of firebricks, which

are continued up to the throat, A, of the furnace: the whole is cased in solid masonry, E, E, and supported by iron bands. When working regularly, such a furnace is charged through the opening, B, near the top, at intervals, first with coal, and then with a suitable mixture of roasted ore and of a limestone flux broken into small fragments. As the fuel burns away, and the materials sink down gradually, fresh layers of fuel, and of ore and flux, are added; so that the furnace becomes filled with alternate layers of each.

The principal substances which are acted upon in such a furnace are the following:—

1st, the oxygen contained in the air of the blast; 2nd, the roasted ore,—consisting of oxide of iron, silica in the shape of sand or quartz, clay or aluminic silicate, and a little magnesia and oxide of manganese; 3rd, coal or coke,—composed chiefly of carbon, with a small proportion of hydrogen; and 4th, calcic carbonate or limestone, which in the heat of the furnace soon becomes quicklime.

(745) *Theory of the Blast Furnace.*—The chemical changes may be traced as follows, beginning at the bottom of the furnace:—The oxygen contained in the air of the blast, as soon as it comes into contact with the fuel in the crucible, combines with the carbon and forms carbonic anhydride, attended with a combustion of intense activity. The blast is thus soon deprived of all its free oxygen; nearly the whole of the nitrogen escapes unchanged, but the carbonic anhydride, in its passage over the ignited fuel, is decomposed; each atom of the anhydride combines with an additional atom of carbon, and becomes converted into carbonic oxide; for each volume of carbonic anhydride 2 volumes of carbonic oxide are produced. This formation of carbonic oxide is attended with a large absorption of heat, so that the temperature of the furnace, above the crucible, becomes rapidly reduced, and a quantity of highly combustible gas is thus formed.\* This car-

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\* Bunsen and Playfair, in their examination of the gases produced in a hot-blast furnace at Alfreton, found that a considerable amount of potassic cyanide was formed in the hotter portions of the furnace (*British Association Reports*, 1845, p. 182): part of the nitrogen, derived probably both from the blast and from the coal, had therefore entered into combination with carbon, and had united with the potassium contained in small quantities in the ore and in the ashes of the coal.

The furnace in which these experiments were made was 12 metres, or 40 feet deep from the top of the charge to the hearthstone, and was charged every twenty minutes with 420 lb. of calcined clay ironstone, containing about 60 per cent. of oxide of iron, 390 lb. of coal, and 170 lb. of limestone: each charge

bonic oxide becomes mingled with carburetted hydrogen and free hydrogen, which are derived from the fuel contained in the upper part of the charge, as it gradually descends towards the focus of intense heat below. A proportion of the gases which escape from the opening at the top of the furnace, varying from 35 to 40 per cent., is combustible; the remainder consists principally of nitrogen, with a small amount of carbonic anhydride. The ore having been rendered porous by the previous roasting, is easily penetrated by these ascending gases, by contact with which the iron becomes reduced in the upper part of the boshes, where the heat is comparatively moderate. By degrees the reduced metal, mixed with the earthy matter of the ore, sinks down to the hotter region. Here the earthy matters melt and become vitrified; whilst the iron, in a minutely divided state, being brought into contact with the carbon of the fuel, combines with it and forms the fusible compound well known as cast iron. This carbide of iron melts,

yielded 140 lb. of pig-iron. The blast was under a pressure of 6·75 inches of mercury, and had a temperature of 626° (330° C.)

These chemists state that at a depth of 2½ feet from the tuyère, or 34 feet from the top of the furnace, the gases which they collected contained 1·34 per cent. of cyanogen. The following table furnishes a summary of the results which they obtained:—

*Analysis of Gases from a Hot-blast Furnace.*

Depth from the top Height from tuyère	5 feet. 32	8 29	14 23	17 20	20 17	24 13	34 2½
Nitrogen ...	55·35	54·77	50·95	55·49	60·46	56·75	58·05
Carbonic anhydride	7·77	9·42	9·10	12·43	10·83	10·08	0·00
Carbonic oxide ...	25·97	20·24	19·32	18·77	19·48	25·19	37·43
Marsh gas ...	3·75	8·23	6·64	4·31	4·40	2·33	0·00
Hydrogen ...	6·73	6·49	12·42	7·62	4·83	5·65	3·18
Olefiant gas ...	0·43	0·85	1·57	1·38	0·00	0·00	0·00
Cyanogen ...	0·00	0·00	0·00	0·00	0·00	trace.	1·34
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

The process of coking, which is effected in the upper part of the furnace, did not appear to be complete until the charge had reached a depth of 24 feet, but was most active at a depth of 14 feet; the principal reduction of the ore seemed to take place just below the point at which the coking was completed: the maximum heat of this furnace occurring at about 1 metre, or between 3 and 4 feet above the tuyère, or 33 feet from the top.

In a furnace fed with charcoal, Bunsen found the reduction of the ore to commence nearer the throat of the furnace, for in this case no absorption of heat occurred similar to that occasioned by the process of coking the coal, which takes place in the upper part of the hot-blast furnace. The body of a charcoal furnace consequently does not require to be so high as that of a furnace in which coal is used. Similar experiments by Ebelmen lead to conclusions substantially the same.

sinks down below the tuyères, through the lighter vitrified slags, and is protected by them from the further action of oxygen. The bulk of the slag is 5 or 6 times as great as that of the iron produced: it floats above the melted metal, and is allowed to flow over continually at the opening left for the purpose; whilst the iron is run off at intervals of 12 or 24 hours, by withdrawing the stopping of clay and sand from the tap-hole at the bottom.

The furnace slags constitute an imperfect species of glass, which is sometimes more or less distinctly crystalline, and which varies in colour with its composition, being usually opaque and grey, but often tinged blue, green, brown, or black. They consist principally of calcic, magnesian, and aluminic silicates, with generally a small proportion of manganous and ferrous silicates. In the formation of these slags the siliceous matters of the ore react upon the earthy bases, lime, magnesia, and alumina, and really neutralize them.

The general composition of these slags may be seen from the subjoined analyses: I. A slag obtained from Merthyr Tydvil, by Berthier. II. A cold-blast slag, Tipton, Staffordshire, by D. Forbes. III. A hot-blast slag from coke-furnace, by Percy. IV. Average of slag from 13 blast-furnaces at Dowlais, by Riley; the last three quoted from Percy's *Metallurgy*, vol. ii. pp. 497 and 499.

Constituents.	I.	II.	III.	IV.
Silica ... ..	40·4	39·52	37·91	43·07
Alumina ... ..	11·2	15·11	13·01	14·85
Ferrous oxide ... ..	3·8	2·02	0·93	2·53
Manganous oxide ... ..		2·89	2·79	1·37
Lime ... ..	38·5	32·52	31·43	28·92
Magnesia ... ..	5·2	3·49	7·24	5·87
Potash ... ..		1·06	2·60	1·84
Calcic sulphide ... ..	traces	2·15	3·65	1·90
Phosphoric anhydride ... ..				traces
	99·1	98·76	99·56	100·35

The oxygen in the bases of these slags is nearly equal in amount to that contained in the silica. Those quoted from Percy approach the formula,  $[12(\text{CaMgMnFe})\text{O}], 2\text{Al}_2\text{O}_3, 9\text{SiO}_2$ .

The composition of No. I. may be represented by the formula,  $[15(\text{CaMgFe})\text{O}], 2\text{Al}_2\text{O}_3, 11\text{SiO}_2$ .

There are several points which require nice adjustment in this process of reduction. The slag must not be of too fusible a description, otherwise the iron falls to the bottom before it has



thoroughly combined with the carbon, and is not completely melted; a sufficiency of lime should always be present to neutralize the whole of the silica, for unless this be attended to, a ferrous silicate is formed, and iron runs off in waste. Indeed, a small excess of lime is advantageous, as it removes sulphur, if present, in the shape of calcic sulphide. At the same time the calcareous matter must not be too abundant, otherwise the working of the furnace is obstructed; the slags which are formed being of a less fusible character are but imperfectly melted, the iron is entangled within them, it is again partially oxidated by the blast, and the product of the furnace is greatly diminished. Experience has shown that the slags (which are chiefly composed of the mixed calcic and aluminic silicates) are most fusible when the oxygen of the silica amounts to double that in the bases with which it is combined, and when the proportion of lime employed is such as would be furnished by adding 2 parts of limestone for every 3 of clay contained in the ore; the ratio of lime to alumina being  $6\text{CaO} : \text{Al}_2\text{O}_3$ . The lime is here said to act as a flux, (from *fluo*, to flow,) or material used to liquefy the clay. A slag of this kind, however, can only advantageously be formed when the ore is smelted with charcoal, a fuel which contains but little sulphur, and which allows the reduction to be effected at a comparatively moderate temperature. When coal or coke is used as the fuel, an excess of lime is required to carry off the sulphur introduced by the pyrites of the coal, and the slag which is produced under these circumstances is found to work most advantageously when the proportion of oxygen in the bases is nearly equal to that of the silica. The temperature of a blast furnace fed with coal or coke is much higher than that of one in which charcoal is used. Slags containing several bases are more fusible than when one or two only are present, the different silicates aiding the fusibility of each other. For a summary of an extensive experimental inquiry into the composition and properties of slags, the reader is referred to Percy's *Metallurgy*, vol. i. pp. 20—49, and vol. ii. p. 497.

In the process of smelting it is also necessary to proportion the supply of air rightly; if too much be thrown in, the furnace becomes unduly cooled; if too little, the supply of oxygen is insufficient for the maintenance of a proper temperature by a due amount of combustion. These, however, are points the successful regulation of which can only be acquired by experience. The stream of air for the blast is not supplied in intermitting gusts, but is equalized as much as possible: where the cold blast is used, this object is attained by employing an air-chamber or reservoir;

and where the hot blast is employed, the long pipes required for heating the air answer the same purpose.

(746) *The Hot Blast*.—The mass of air which passes through one of these furnaces is enormous, being not less than 4750 cubic metres, or about 6000 kilos. (nearly 6 tons weight) per hour. It is evident, therefore, that this immense volume of air must exercise an extraordinary cooling effect upon the contents of the furnace. This evil has been much reduced of late years by the introduction of air which has been previously heated. In this contrivance, which is known as the *hot blast*, the air, before it reaches the furnace, is made to pass through a series of pipes which are maintained at a high temperature, either by means of a separate furnace, or by a portion of the waste heat of the blast furnace itself: in the latter case the hot gases are conveyed through flues which pass from the upper part of the furnace into the chamber which contains the pipes; the necessary draught being maintained by a chimney furnished with a damper. A jet of the blast as it enters the furnace should have a temperature sufficiently high to melt a strip of lead when held in it. The temperature of such a jet as it issues from the tuyère is somewhat higher than  $617^{\circ}$  ( $325^{\circ}$  C.). Mr. Siemens has improved upon this plan by transmitting the gases which escape from the furnace, through what he terms a *regenerator*. It is simply a chamber of brickwork filled with fire-bricks so arranged as to allow the heated gases to circulate freely around them. Two such chambers are prepared; as soon as the bricks in one of these chambers are red-hot, the current of gas from the furnace is cut off, and directed into the other chamber, in order to heat it. In the meantime a current of cold air is forced through the heated chamber, and a hot blast of from  $1200^{\circ}$  to  $1300^{\circ}$  ( $650^{\circ}$  to  $704^{\circ}$  C.) is thus obtained. Each chamber is worked alternately; the one becoming heated whilst the other is employed in heating the blast. In this way a large proportion of the heat of the waste gases may be economized.\*

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\* This process, as its value becomes appreciated, will no doubt come into very extensive use in a great variety of operations in metallurgy. In many cases it effects an economy of one-half of the fuel employed, and it is possible to obtain by its means a steady and uniform temperature from one not exceeding that of a full red, up to the heat required for welding iron. It is now employed with great success both in glass-making and in welding the joints of wrought-iron tubes. Mr. Siemens prefers to distil the coal in furnaces through which a regulated supply of air is transmitted, thus furnishing a mixture of gaseous hydrocarbons with carbonic oxide and the nitrogen of the spent atmospheric air, and these combustible gases are conveyed by a flue and burned at the spot where the heat is required. The gases after having done their work are passed

The saving of fuel effected by the employment of the hot blast is immense, and is much greater than was at first anticipated:  $2\frac{3}{4}$  tons of coal are now amply sufficient for the production of a ton of iron, from ore which would have required 8 tons when the cold blast was used. This saving is effected owing to the operation of several causes, one of which is, that raw coal may now be used in the furnace instead of coke: moreover, as a smaller quantity of fuel is required in the furnace to raise the injected air to the necessary temperature, so also a smaller quantity of air is needed to maintain the combustion: combustion takes place within a shorter time, so that the maximum heat of the furnace is obtained lower down in the 'crucible,' and the upper portions of the furnace do not become so intensely heated: the reduction of the ore consequently takes place nearer to the bottom, and the heat is thus concentrated and economized. Further:—

In every metallurgical process a particular temperature must be attained in order to secure the occurrence of the reaction, or of the fusion which is desired. All fuel consumed at temperatures below that point is ineffective, and is therefore burned to waste. It must be remembered that in every case of combustion where the same chemical compounds are produced, a definite weight of fuel always emits a definite amount of heat; consequently it will raise a definite weight of air, and of materials in the furnace, through a definite number of degrees of temperature:—Say that a certain weight of fuel will raise the temperature of a given charge in the furnace from  $59^{\circ}$  to  $2579^{\circ}$  ( $15^{\circ}$  to  $1415^{\circ}$  C.). Now, the same weight of fuel (if we neglect the quantity of heat absorbed by alteration of the specific heat with rise of temperature) will also raise the same charge from  $662^{\circ}$  to  $3182^{\circ}$  ( $350^{\circ}$  to  $1750^{\circ}$  C.). Suppose, now, that iron required a temperature of  $2732^{\circ}$  ( $1500^{\circ}$  C.) for its fusion, no amount of fuel burned so as to produce a temperature of  $1415^{\circ}$  C. would be of any avail in effecting the fusion of the metal, whilst a comparatively small quantity, starting from the initial temperature of  $350^{\circ}$  C. would produce the desired result.

Even in a hot-blast furnace, however, the quantity of fuel which is wasted is enormous. Bunsen and Playfair, from their elaborate experiments at Alfreton, make the almost incredible estimate that

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through the regenerator above described; and in the furnace where the combustion is effected, a temperature can thus be obtained, limited at present only by the powers of the fire-brick to resist its fusing action. The gas furnace, for such it is, has already, in some cases, superseded the old coal furnace in glass-making.

somewhat more than four-fifths of the total quantity of heat producible from the fuel consumed is lost, owing to the escape of unburned combustible matter in the form of gases, such as carbonic oxide, carburetted hydrogen, and hydrogen, which are still fit for use. Since the publication of these researches, Mr. Budd and other ironmasters have economized a portion of the heat contained in the escaping gases, in heating the blast and in generating steam.

The iron obtained by the use of the hot blast is inferior in tenacity to cold-blast iron; a circumstance which appears to be partially due to the fact that the proportion of silicon is greater in hot- than in cold-blast iron; it is also to be noticed, that in the employment of the hot blast uncoked coal is used, a fuel which contains more sulphur, and possibly also more phosphorus, than coke, which is required in working with the cold blast.

A furnace in full work requires an hourly supply of 1600 kilos., or rather more than  $1\frac{1}{2}$  ton of solid material, consisting of an average of 5 parts of coal, 5 of roasted ore, and 2 of limestone. The roasted clay-iron ore yields on an average 35 per cent. of iron, and each furnace when in full activity furnishes from 8000 to 10,000 kilos., or about 8 or 10 tons of metal in the 24 hours. Every morning and evening it requires to be tapped: on these occasions the iron is run into shallow grooves in the sand, and forms the cast iron, or pig-iron of commerce. A good furnace, if well managed, may be made thus to work uninterruptedly without repair for many years.\*

(747) *Varieties of Cast iron.*—The iron as it runs from the furnace, however, is not a pure carbide or carburet, for in the intense heat, not only is the iron reduced, but portions also of silicon, aluminum, and calcium, and occasionally other bodies derived from the flux and from the fuel. These bodies enter in small quantity into combination with the iron, the properties of which they modify materially. Manganese generally accompanies the ores of iron in greater or less quantity, and frequently com-

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\* The production of iron in Great Britain, in 1865, amounted to about 4,819,254 tons. It was estimated in 1855, by Mr. Blackwell, that the annual production of iron in different countries was then as follows:—

Tons.			Tons.		
England	...	3,000,000	Belgium	...	200,000
France	...	750,000	Russia	...	200,000
North America	...	750,000	Sweden	...	150,000
Prussia	...	300,000	Germany	...	100,000
Austria	...	250,000	Other states	...	300,000

In all, six millions of tons, of which Great Britain supplied one-half.

biner with the reduced metal. Cast iron differs greatly in quality; the differences observed in it depend in part upon differences in the proportion of carbon and silicon which it contains. The composition of these carbides varies considerably within certain limits; but it does not appear that iron is capable of combining with more than about 5 per cent. of carbon. A compound of carbon having the composition of  $\text{Fe}_4\text{C}$ , or the *tetraferrocarbide*, would consist of 94.92 of iron, and 5.08 of carbon; and this is very nearly the composition of the hardest and most fusible kind of white cast iron, which, from the circumstance of its crystallizing in flat brilliant tables, is termed by the Germans *spiegeleisen* (or mirror iron): according to Gurlt, the specific gravity of this carbide is 7.65. *Spiegeleisen* is, however, not a pure carbide of iron, but always contains manganese, in amount varying from 4 to 10 or 12 per cent. Faraday and Stodart found the most highly carburetted iron which they could produce to consist of—iron, 94.36; carbon, 5.64. Gurlt (*Chem. Gaz.*, 1856, p. 231) has described another definite form of cast iron ( $\text{Fe}_8\text{C}$ ), the *octoferrocarbide*, which when pure contains 2.63 per cent. of carbon. It has a sp. gr. 7.75, is of an iron-grey colour, and has a hardness much inferior to that of the tetraferrocarbide, being slightly malleable. It crystallizes in confused octohedral groups, and according to Gurlt is the principal constituent of grey cast iron. The existence of this compound is probable, but cannot be regarded as absolutely proved. In many varieties of cast iron the carbon exists in two distinct forms,—one portion being chemically combined with the metal, the other being mechanically diffused through it in the condition of graphite, the scales of which may be seen distinctly with a magnifying lens, when the surface of a freshly fractured bar is examined. These scales remain unacted upon when the metal is dissolved in diluted acids; the combined carbon under such circumstances unites with hydrogen, and forms an oily-looking liquid of ill odour.

In addition to carbon, cast iron also contains silicon, the proportion of which is equally liable to variation; the quantities of silicon which have been found in pig-iron range between 3.5 and 0.25 per cent.

Karsten found that when cast-iron was melted with sulphur in a covered clay crucible, there was formed, on cooling, a layer of ferrous sulphide upon the surface, then a layer of graphite, and beneath this a layer of carbide of iron in the maximum degree of carburization. These effects may be thus explained:—Carbon is incapable of decomposing ferrous sulphide, but sulphur can displace carbon from the carbide. On the addition of sulphur to the melted cast iron the carbon gradually becomes concentrated in that part of the iron not com-

bined with the sulphur, until its point of saturation with carbon is reached, and then the graphite is separated. According to the same authority, both phosphorus and silicon act in a similar manner, phosphide and silicide of iron being formed, whilst the carbon becomes concentrated in the remainder until the excess of carbon is expelled and crystallizes in the form of graphite. When the proportion of phosphorus, of silicon, or of sulphur, is but small, the compounds which they form with the iron remain disseminated through the mass of cast iron, and exert an important influence upon its texture and tenacity.

According to Le Guen (*Ann. de Chimie*, III. lxi. 282), if good grey pig-iron be fused with  $2\frac{1}{2}$  per cent. of powdered wolfram, the cast iron so produced is rendered much stronger and more elastic, the tenacity being increased from 3 to 4: if the quantity of wolfram be increased to 3 per cent. the metal becomes still harder, but not so tough. It is however doubtful whether the wolfram acts otherwise than as a flux, which facilitates the fusion of the iron and separation of some of its impurities.

The following table will serve to illustrate the general composition of some varieties of cast iron:—

	Gurtl.			Bodemann.		Abel.	
	Grey coal.	Mottled hot blast.	White Gartsherrie.	Grey hot blast.	Mottled cold blast.	Grey French charcoal.	White Silesian, very crys.
Specific gravity ...	7.21	7.21	7.41	7.166	7.43	7.000	7.531
Carbon, combined ...	1.021	1.793	2.457	1.44	2.78	...	4.94
Graphite ...	2.641	1.110	0.871	2.71	1.99	3.40	...
Silicon ...	3.061	2.165	1.124	3.21	0.71	0.80	0.75
Sulphur ...	1.139	1.480	2.516	trace	trace	0.05	trace
Phosphorus ...	0.928	1.171	0.913	1.22	1.23	0.45	0.12
Iron ...	90.236	89.314	89.863	91.42	93.29	95.18	88.57
Manganese ...	0.834	1.596	2.715	trace	trace	...	5.38
Copper ...	...	...	...	...	...	...	0.24
Arsenicum ...	...	...	...	...	...	trace	...
Cobalt ...	...	...	...	...	...	...	trace
Chromium ...	...	...	...	...	...	trace	...
	99.860	98.629	100.459	100.00	100.00	99.88	100.00

Gurtl's specimens were all made in the same furnace, and with the same material; the grey at the highest temperature, the white at the lowest.

The fusing-point of cast iron varies with its composition; that of an average specimen was estimated by Daniell at  $2786^{\circ}$  ( $1530^{\circ}$  C.).

In commerce there are three principal varieties of *cast iron*, known respectively as *grey* cast iron; *mottled* cast iron; and *white* cast iron. The first two contain carbon disseminated in an uncombined form through the mass. Grey cast iron is soft; it may be filed, drilled, and turned in the lathe, and though somewhat less fusible than the white, is preferred for casting, since when melted its liquidity is more perfect. This variety is that which is generally produced from a furnace in good working order; if

cooled suddenly, it is often converted into hard white cast iron. This circumstance is taken advantage of in preparing *chilled shot*, which are cast from a fusible grey iron in a cold mould, and acquire great hardness upon the surface. The dark-grey iron used for castings, and termed *foundry iron*, requires the presence of more carbon than the lighter variety, or *forge iron*, used for conversion into wrought iron. The fracture of the *mottled* variety is in large coarse grains, among which points of graphite are distinctly visible; it is very tough, and is valued for casting ordnance. It may be obtained for this purpose by partially refining good grey iron. *White* cast iron contains about the same amount of carbon as the mottled iron, but the whole of the carbon appears to be chemically combined with the metal. The white variety passes through a pasty condition as a preliminary to liquefaction; it is more fusible than either of the others, is lighter in colour, very hard and brittle, has a lamellar crystalline fracture, and a specific gravity varying between 7.2 and 7.6. It usually contains less silicon, but more sulphur and phosphorus than grey iron. White cast iron seems in some cases to owe its colour to the presence of manganese. A much higher temperature in the furnace, and consequently a greater consumption of fuel is required for the production of grey than of white iron. This may probably arise from the fact, that if white iron be melted and exposed to a temperature considerably higher than its melting-point, the tetra-ferrocarbide is decomposed, and if it be allowed to cool very gradually, a portion of the carbon crystallizes out as graphite, and grey cast iron is produced. In the process of casting heavy articles this carbon separates, and is thrown off in the form of brilliant scales, termed by the casters *kish*.

The peculiar value of iron for castings depends upon its property of expanding at the moment of solidification. It thus furnishes an admirable material for taking the most minute impressions, as is well exemplified in the beautiful castings obtained from Berlin.

Small articles made of cast iron, such as key-blocks, stirrup-irons, &c., may be rendered malleable by packing them in powdered hæmatite, then heating them to redness for some hours, and allowing them to cool very slowly.\* In this case the oxygen of the oxide removes a portion of the carbon by a process of cementation the reverse of that which takes place during the manufacture of steel: the

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\* The samples analysed by myself, and the results of which were quoted in former editions of this work, were supposed to have been obtained from the *same* iron, but were not really so; no correct conclusions can therefore be drawn from the comparison of the two analyses, which seemed to indicate the withdrawal of silicon as well as carbon.

carbon is gradually removed from the outer layer of the metal, and is slowly transmitted from particle to particle through the solid bar, till it reaches the surface, where it undergoes oxidation at the expense of part of the oxygen of the hæmatite.

(748) *Conversion of Cast iron into Wrought iron.*—I. *Refining.*

—The pig-iron as delivered from the furnace is, as already noticed, far from pure: it contains variable quantities of carbon, silicon, sulphur, and phosphorus, besides traces of other metals, such as aluminum, calcium, and potassium. Before it can be converted into the wrought iron of commerce, it has to undergo a process for the removal of these extraneous matters. Many castings may be made at once with pig-iron, but it cannot be worked at the forge.

In order to effect the purification of the crude pig-iron, it is necessary to expose it to the regulated action of oxygen at a high temperature, so as gradually to burn off these oxidizable substances, and leave the iron. The pig iron is usually first remelted in quantities of from 25 to 30 cwt., upon the hearth of a sort of forge, termed the *finery* or *refinery*, the fire of which is animated by a cold blast from a double row of blast-pipes. The sides and back of the hearth are formed of hollow iron castings, through which water is kept continually flowing. During this operation, which lasts about two hours, and is one of the most wasteful both of fuel and of iron, the metal loses from 10 to 12 per cent. of its weight. The silicon is more readily oxidized than the carbon, so that it is the impurity which is first attacked in the refining process, but at the same time a small portion of the carbon contained in the iron is burned off as carbonic oxide; part of the iron also becomes converted into the protoxide, which unites with the silica furnished by the oxidation of the silicon, and with the sand which adhered to the surface of the cast metal: a fusible slag consisting of ferrous ortho-silicate ( $2\text{FeO}, \text{SiO}_2$  or  $\text{Fe}''_2\text{SiO}_4$ ) is thus produced. The oxide of iron in this slag again reacts upon the melted metal, and by imparting a portion of its oxygen to the silicon and carbon disseminated through the mass, burns off an additional quantity of these substances; portions of sulphur and phosphorus are also separated by oxidation in this process, and accumulate in the slag. The melted iron is then run off, and formed into a flat cake 2 or 3 inches (from about 5 to 8 centimetres) thick, and as soon as it begins to solidify it is suddenly cooled by pouring water upon it; a hard white, brittle mass is thus obtained, which is broken up into fragments. In this operation coke is the combustible generally made use of, but where iron of superior quality is required, as in making tin-plate, charcoal is employed. Ord-



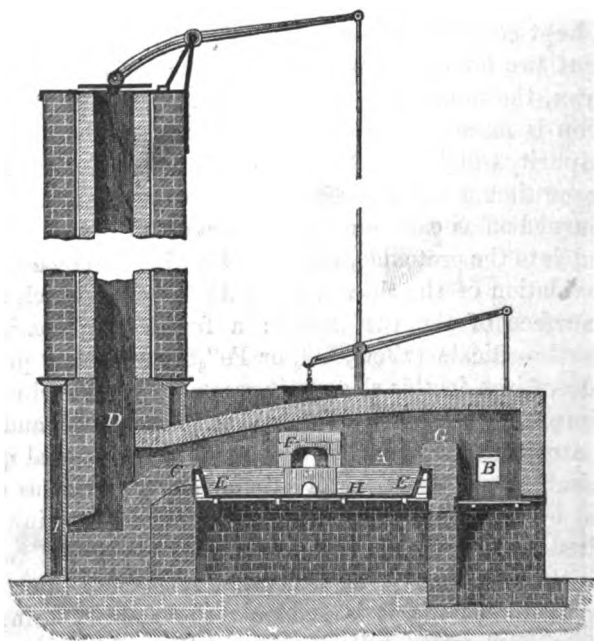
nary coke contains sulphur and earthy impurities which injure the quality of the iron.

The effect of the operation is well exhibited by the following analysis quoted by Regnault, giving the composition of a portion of cast iron before refining, and a portion of the same metal after it had passed through the refinery furnace.

	Before refining.	After refining.
Carbon ... ..	3'0	1'7
Silicon ... ..	4'5	0'5
Phosphorus ... ..	0'2	
Iron ... ..	92'3	97'8
	100'0	100'0

(749) *Puddling*.—The refined metal still retains a considerable proportion of carbon and some silicon. In order to remove them it is next introduced, in charges of from 4 to 5 cwt., or about 250 kilos., into the *puddling furnace*. This consists of a reverbe-

FIG. 356.



ratory furnace, connected with a chimney 40 or 50 feet (12 or 15 metres) in height, and capable of producing a powerful draught, which is under complete command by means of a damper.

Fig. 356 represents a section of the puddling furnace; A, is the bed, or hearth, upon which the iron for puddling is placed; B, is the fire-place with the aperture for stoking, which is closed with coal, and not by a door, as is usual in most furnaces: C, is the bridge which separates the fuel from the metal: the hearth, A, is lined with cast-iron plates, E, E, which are prevented from melting by the free circulation of air beneath them; D, is the flue leading to the chimney, N, at the top of which the damper is shown; H, is the plate upon which the iron rests during the puddling process; it is protected from the heat by a coating of powdered hæmatite, of sand, or of slag;\* R, is the working door of the furnace through the upper aperture in which the puddler works; the lower aperture is closed by sand during the operation, and is opened at intervals to allow the slag or *tap cinder* to be drawn off, and I is the *floss-hole*, or aperture through which the overflow of slag is removed.

For the coarser kinds of iron the furnace is sometimes charged partially, or even wholly, with pig-iron that has not been refined. Iron which has undergone the refining process never becomes so completely liquid in puddling as when crude pig-iron is employed, but the product is a metal of finer quality.

Supposing the crude pig-iron to be used, the pigs slowly become melted, and the metal when first heated forms a thick pasty mass, which gradually becomes fluid, and at length perfectly liquid. At this stage the metal becomes violently agitated, owing to the escape of the carbonic oxide in jets, which take fire and burn with a blue flame, whilst the melted mass swells up to several times its original bulk: this process is technically known as *boiling*. The melted iron is now briskly stirred by the puddler to promote oxidation.

When refined iron is used in puddling instead of crude iron, it is often mixed with a certain proportion of scales of oxide from the forge, and is then gradually brought into complete fusion, carefully avoiding the contact of fuel. The mass is well stirred, so as to incorporate the oxide of iron with the melted metal; oxygen is transferred from the oxide thus introduced to the carbon of the melted iron, and carbonic oxide is formed abundantly; but the appearance of boiling is less marked than when crude pig-iron is used. In either case, the metal by degrees

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\* The employment of lime as a lining to the furnace has been recommended; it is said to improve the quality of the iron by removing sulphur more completely, and at the same time to diminish the rate of oxidation.

becomes less fusible as the carbon diminishes in quantity, and at length it is converted into a granular, sandy mass. The heat is now raised till it becomes very intense, and air is carefully excluded by closing the damper and doors. The metal again begins to soften and agglomerate. The puddler gradually collects it into balls or *blooms* upon the end of an iron rod; he then removes it from the furnace in masses weighing about three-quarters of a hundredweight, or 38 kilos., and subjects it, whilst still intensely hot, to the action either of the steam hammer or of a powerful press, called the *shingling press*. The melted slag is thus forcibly squeezed out, the particles of metal are brought nearer together, and the density is increased. The iron is then fashioned into a bar by passing it between grooved rollers, and the bar thus obtained is cut into lengths, then piled up in a reverberatory furnace and re-heated; it is again rolled, doubled upon itself, and re-heated and rolled. Upon the best qualities of iron this process is repeated several times, in order to render its fibres parallel to each other, by which the toughness of the metal is much increased. The iron is now nearly pure; it contains from  $\frac{1}{100}$  to  $\frac{1}{1000}$  of its weight of carbon, and about  $\frac{1}{100}$  of silicon. The presence even of this small proportion of carbon adds materially to the toughness and hardness of the metal. The process of puddling occupies about two hours; and provided it has been properly refined previously, the metal loses from 7 to 10 per cent. of its weight.\*

\* Calvert and Johnson (*Phil. Mag.* Sept. 1857) have made a series of analyses of the iron in different stages of the process of *boiling*. They employed in their experiments good cold-blast Staffordshire grey iron, No. 3, such as is used for making iron wire.

		Time after charging.	Carbon.	Silicon.	Phos- phorus.	Sulphur.
Pig iron ...	...		2.275	2.720	0.645	0.301
1st sample	...	40'	2.726	0.915		
2nd "	...	60'	2.905	0.197		
3rd "	...	65'	2.444	0.194		
4th "	...	80'	2.305	0.182		
5th "	...	95'	1.647	0.183		
6th "	...	100'	1.266	0.163		
7th "	...	105'	0.963	0.163		
8th "	...	110'	0.772	0.168		
9 Puddled bar	...		0.296	0.120	0.139	0.134
10 Wire iron	...		0.111	0.088	0.117	0.094

A charge of 2 cwt. of iron was introduced into the bed of the furnace without any addition of oxide of iron: in 40 minutes it became fused, and on cooling the sample suddenly, it yielded a brittle mass like white iron. It will be seen

The slag produced during the operations of puddling and refining consists chiefly of ferrous ortho-silicate ( $2\text{FeO}, \text{SiO}_2$ ) and contains upwards of 60 per cent. of the metal. This slag or *finery cinder* is reduced in the blast furnace in the same manner as the original ore, but it is always found to produce a defective iron, technically known as *cold short*. Such iron may be forged well at a red heat, but when cold it is brittle and rotten. This defect is attributed to the presence of phosphorus, which is separated from the crude metal in the form of phosphate of iron during the puddling. When the slag is reduced in the blast furnace, both the phosphorus and the iron are deprived of their oxygen, and by their union, as phosphide of iron, form the faulty metal in question.

Mr. Bessemer has attempted to substitute for the processes of puddling and refining a method of purification which consists in forcing cold air at a pressure of 12 or 16 lb. upon the square inch through melted cast iron, 3 or 4 tons of which, as it runs from the furnace, is received into a cylindrical vessel covered with an arched head and lined with a coarse siliceous rock, termed *ganister*; this is crushed, moistened with water, and applied to the interior where it dries slowly; during the smelting the air is driven in at the bottom, through several tuyères. An intense combustion occurs, attended with remarkable elevation of temperature, owing partly to the oxidation of the iron, and partly to that of the carbon; the latter, being converted into carbonic

that whilst the carbon increases during the first stage of the process, the silicon undergoes a very rapid diminution. The 3rd sample was taken just before the beginning of the *boil*, when the iron was in its most fluid condition. No. 4 was taken during the full boil, and consisted of small detached brittle granules surrounded by slag. No. 5 the boil was completed. It was still in granules, but they were slightly malleable. No. 6, the iron was collecting into masses. No. 7 was taken during balling, and in No. 8 the balls were just ready for the shingling press. The 'puddled bar' was taken from the iron after it had been hammered; and the 'wire iron' was the same after it had been broken up into billets, reheated, and rolled as a preliminary to drawing.

The slag which was separated during the operation was found to have the following composition:—

Silica	...	...	...	...	...	16.53
Ferrous oxide	...	...	...	...	...	66.23
Ferrous sulphide	...	...	...	...	...	6.80
Phosphoric anhydride ( $\text{P}_2\text{O}_5$ )	...	...	...	...	...	3.80
Manganous oxide	...	...	...	...	...	4.90
Alumina	...	...	...	...	...	1.04
Lime	...	...	...	...	...	0.70

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100.00

oxide, escapes at all points of the mass, throwing the whole into violent agitation, which subsides as soon as the carbon is burnt off, generally at the end of about 15 minutes ; when this occurs the melted iron nearly freed from carbon is run off into moulds. A great loss of iron is, however, incurred in this operation ; a copious slag of oxide of iron, mixed with a little silicate, is produced, and in this a large quantity of metallic iron is entangled : not less than 20 per cent. of the metal is thus wasted, and the malleable iron still retains nearly all the phosphorus and much of the sulphur originally present.

But though the process of Bessemer has not been attended with the important results which were anticipated from its employment in refining the ordinary pig-iron obtained by the smelting of clay iron-stone with coal, it has been eminently successful when applied to the pure Swedish charcoal pig-iron, and to the Lancashire hæmatite pig, which have by its means been converted by a single operation of short duration into cast steel of the finest quality : as much as 5 tons of iron are commonly operated on at one fusion. Bessemer steel is now commonly made by adding to the melted wrought iron, just before pouring, a definite quantity of white cast iron of known composition, usually containing about 6 per cent. of carbon and 10 of manganese, by which means the requisite amount of carbon is combined with the iron, and steel of the required quality is obtained (751). It is then immediately run into ingots.

(750) *Production of Wrought Iron direct from the Ore.*—The pure ores, which consist of magnetic oxide, or of ferric oxide, are frequently converted at once into wrought iron, without the production of cast iron. This process is practised in the Pyrenees, by what is termed the Catalan forge, and still more largely by the *bloomery forges* of North America. In the American bloomery forge either the hot or the cold blast may be employed :—The ore having been first reduced by stampers to a coarse powder, is placed on the top of the coal in the forge which has been kindled for its reception ; a high heap of coal is kept on the fire, and a gradual supply of ore is maintained ; as the metal is reduced, it sinks to the bottom in a pasty state ; when sufficient has been added to form a bloom, or ball, the metal is collected on an iron bar, heated before the blast-pipe, and then hammered, rolled, and welded, as if it had come from the puddling furnace (Overman's *Metallurgy*, p. 544). This method yields a very pure iron when charcoal is employed, but the consumption of fuel per ton of metal is much greater than in the blast-furnace ; a large portion of the

ore is also wasted in the form of slags, which are very rich in oxide of iron. The iron produced by this process frequently contains sufficient carbon to give to it some of the properties of steel; for instance, it becomes much harder when heated and suddenly cooled. Iron of this description is valuable in the manufacture of plough-shares, and heavy articles requiring both toughness and hardness.

(751) *Manufacture of Steel*.—Iron, when combined with a smaller proportion of carbon than is contained in cast iron, furnishes the valuable compound well known as *steel*, of which there are several varieties. The quantity of carbon in good steel varies between 0·7 and 1·7 per cent.; but steel which possesses the greatest tenacity has been found to contain from 1·3 to 1·5 per cent. of carbon, and about 0·1 of silicon. *Natural steel* is produced directly from the best cast iron by heating it by means of charcoal on the refining hearth, as in the operation which precedes the process of puddling; the oxygen burns off a portion of the carbon from the cast iron, and steel is left. In some of the Welsh ironworks steel is now made upon the bed of the puddling furnace itself, by carefully arresting the operation at a stage short of the complete oxidation of the carbon. The preparation of natural or puddled steel is, therefore, an intermediate stage in the conversion of cast into wrought iron. Iron which contains manganese is best fitted for the preparation of this kind of steel. The mass thus obtained is rendered homogeneous by forging. It yields a steel of inferior quality, which is employed for making agricultural implements and springs for machinery. *Krupp's cast steel*, made at Essen, near Cologne, is a puddled steel, containing about 1·2 per cent. of carbon. Castings of 16 tons in weight have been obtained for ordnance by pouring steel melted with a little bar iron in crucibles, each holding 30 lb., into the mould, 1200 such crucibles being required for one such casting, which is allowed to cool very slowly in the mould: this is sometimes not opened for 10 or 12 weeks.

For more delicate purposes *blistered steel* is made use of: this is obtained by means of *cementation*, which is an operation just the reverse of that by which natural steel is formed. This process is carried on in a furnace into which are built two rectangular boxes of brickwork or stoneware, for the reception of the bars of iron which are to be converted into steel; the fire-grate is between these boxes, around which the flame circulates freely. This conversion is effected by heating the iron in contact with powdered charcoal, or with soot, forming what is technically termed *cement powder*.

In preparing a charge, the bottom of each box is covered with a layer of the cement powder to a depth of about an inch ( $25^{\text{mm}}$ ), and upon this a layer of bars of the best malleable iron is placed. The bars are generally about 3 inches ( $75^{\text{mm}}$ ) broad, and  $\frac{3}{4}$  inch ( $18^{\text{mm}}$ ) thick. The interstices between the bars are also filled with charcoal powder, which is tightly packed around the iron; above this is a layer of the powder, then another layer of bars, and so on in succession until the box is nearly full, when it contains from 5 to 6 tons of iron. The remaining space is now covered with a layer of damp sand of from 3 to 6 inches (8 to  $15^{\text{cm}}$ ) in depth, and the fire is gradually raised to a full red heat, or to about the temperature required for melting copper,  $1996^{\circ}$  ( $1091^{\circ}\text{C.}$ ); at this point it is steadily maintained. One of the bars of iron is so placed that it can be removed from time to time during the operation, for the purpose of ascertaining the process of the carburization by inspection. The process is usually complete in six or eight days; but the time required necessarily varies with the thickness of the iron bars operated on: the fire is then gradually reduced, and the furnace is suffered to cool slowly, an operation which lasts ten days or a fortnight. The steel thus obtained retains the form of the iron, but it is covered with blebs or blisters, by which the surface is rendered irregular and uneven. The mass is found to have been penetrated by carbon which has been transferred from particle to particle of the metal, the properties of which it has completely changed. In some cases these blisters probably arise from the combination of parts of the carbon with oxygen derived from particles of oxide of iron, which are apt to be mechanically retained even in the most carefully prepared bars. Carbonic oxide would thus be produced, and imprisoned in the tenacious metal, which in its softened state would be raised by it into bubbles or blebs. Great care, however, is generally taken to exclude slag and oxide of iron from bars which it is intended to convert into steel: so that in the majority of instances it is not unlikely that the blisters are occasioned by the combination of carbon with the sulphur which is still retained by the iron, and which, by forming the volatile carbonic disulphide, would produce the effect (T. H. Henry). All bar iron contains traces of sulphur; but in steel sulphur is seldom present, and there appears to be no other mode of accounting for its general absence than its removal during the process of carburization in the form of carbonic disulphide.

By the process of cementation the iron has been combined with about 1.5 per cent. of carbon: it is now much more fusible

than before.\* It has likewise entirely lost its fibrous texture ; and when broken across exhibits a close, fine-grained fracture. Steel may also be made without direct contact with carbon, by simply heating the bars in carburetted hydrogen ; but this process has not come into general use. Graham has shown that iron has the power when heated to redness of absorbing or *occluding* 6 or 8 times its volume of carbonic oxide, which it retains on cooling. No doubt this power of absorbing the gas is intimately connected with the process of cementation (70 a).

Blistered steel is never homogeneous, the surface being always more highly carburetted than the inner portions of the bars. This variety of steel is employed for files, tools, and hardware of all descriptions. When blistered steel is fused, it forms *cast steel*, which, from being more uniform in texture, is of superior quality, as the carbon is more equally distributed throughout the mass : it is employed for cutlery of the best description. *Tilted steel* is also obtained from blistered steel ; this is first broken up into lengths of about 18 inches (or 45<sup>cm.</sup>), then bound into fagots and raised to a welding heat in a wind furnace, where it is covered with sand, which combines with the superficial coating of oxide of iron and forms a fusible slag : the red-hot fagot is then rolled and forged, by means of the tilt-hammer, into smaller bars. All steel is improved by this process of hammering : the tilt hammer weighs about 2 cwt., and strikes 200 or 300 blows per minute. These tilted bars, when broken up and welded together, form *shear steel*.

For many purposes, the addition of a small quantity of manganese is an improvement to the quality of the steel. If about 1 per cent. of carbide of manganese, or of a mixture of charcoal

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\* According to Fremy, steel contains also as a necessary ingredient a minute quantity of nitrogen, which it has been suggested may be in the form of cyanogen. Caron, however, maintains that this trace of nitrogen is not essential. Rammelsberg was unable to detect more nitrogen than 20 parts in a million of cast iron. Marehand heated both cast iron and steel with potassium in an atmosphere of hydrogen, and also heated the metal with soda-lime : he also burned the metal by heating it with cupric oxide, but did not obtain more than 150 parts of nitrogen from a million parts of the metal, and often a much smaller quantity. He considered the nitrogen to be due to the accidental presence of foreign impurities ; and this is certainly the most probable opinion ; no instance is known in which so minute a quantity of matter is an essential constituent of any compound. Bousisingault found pure iron reduced from the oxide in hydrogen gave no trace of nitrogen, by a method of analysis which indicated in soft iron 50 millionths, and in piano wire from 70 to 86 millionths, and in cast steel 57 millionths : this steel also contained traces of sulphur. The difficulty of excluding such minute traces of nitrogen in the course of the analysis is extreme, even in the hands of one who, as in this case, is confessedly a master. (See p. 600.)



and black oxide of manganese, be introduced into the melting-pot, a steel is obtained of fine, close grain, which admits of being welded to wrought iron; a property not possessed by ordinary steel. The experiments of Faraday and Stodart led them to the conclusion that the addition of small quantities of chromium, or of rhodium, to good steel, furnished a steel of a superior kind. They found that steel may be alloyed with about a five hundredth of its weight of silver; and with platinum, as well as with rhodium, and with osmium and iridium in all proportions. The combination of 8 or 9 per cent. of tungsten with ordinary steel has been said to yield a material remarkable for hardness and elasticity, but experience does not seem to justify the expectations of its utility. (Percy's *Metallurgy*, vol. ii. p. 193.) A similar remark is also applicable to titanium steel (*Ib.* p. 168). When steel is to be used for the manufacture of dies for coining, the presence of a small proportion of phosphorus is beneficial (Brande).

When diluted nitric acid falls upon steel, a dark grey spot is produced, owing to the solution of the metal in the acid whilst its carbon remains unacted upon: the acid produces a green spot upon iron. Nitric acid acts unequally upon different parts of the surface in certain of the finer varieties of steel, and thus produces a veined appearance, such as was formerly given to the celebrated Damascus blades. The Damascus steel is more highly carburetted than ordinary steel, and if allowed to cool slowly, it separates into layers of two different degrees of carburation (Bréant): hence certain parts, when acted on by diluted acid, leave more carbon than others; the form and direction of these veins vary with the mode of forging adopted.

*Wootz* is a finely damasked, hard cast steel, of excellent quality, which is obtained from India. Faraday found aluminum in a sample of this steel which he analysed, and was disposed to refer its peculiar qualities to the presence of this metal. It appears, however, from the experiments of Henry (*Phil. Mag.*, July, 1852), that aluminum is not always present in wootz. He gives the following as the composition of a bar of genuine Indian wootz, of specific gravity 7·727:—

Carbon	{	combined ...	...	...	...	1·340
		uncombined	...	...	...	0·312
Silicon		...	...	...	...	0·042
Sulphur		...	...	...	...	0·170
Arsenicum		...	...	...	...	0·036
Iron ...		...	...	...	...	98·100
						<hr/> 100·000

Other analysts have also failed in finding aluminum in wootz.

The physical properties of steel differ materially from those of iron. As already mentioned, steel is granular in texture, brittle, and more easily melted than iron. Its most characteristic property, however, consists in its power of assuming a hardness scarcely inferior to that of the diamond when heated to redness and then suddenly cooled by plunging it into water, mercury, or oil. After this treatment it is rendered extremely brittle, and almost perfectly elastic. It can then no longer be attacked by the file.

This extreme hardness and brittleness may be removed by the process of *tempering*, which is a peculiar mode of annealing; it consists in heating the steel moderately, and then allowing it to cool. The tempering of steel is an operation of great practical importance, as from the variety of purposes to which steel is applied, it is required of very different degrees of hardness, and upon the due adjustment of this quality much of its utility depends. The degree to which the temperature is raised in the second heating, regulates this point: the higher the heat, the softer is the steel. In practice, the workman judges with sufficient accuracy of the temperature to which the metal has been exposed, by observing the colour which the steel assumes owing to the varying thickness of the film of oxide which is formed upon its surface.

The first perceptible tint is a light straw colour, which is produced by the lowest degree of heat, and indicates the hardest temper; the heat required is from  $428^{\circ}$  to  $446^{\circ}$  ( $220^{\circ}$  to  $230^{\circ}$  C.); it is used for lancets, razors, and surgical instruments: at  $473^{\circ}$  ( $245^{\circ}$  C.) a full yellow is produced; it is the temper fitted for scalpels, penknives, and fine cutlery. The temperature of  $491^{\circ}$  ( $255^{\circ}$  C.) gives a brown-yellow, which is the temper for shears intended for cutting iron. At  $509^{\circ}$  ( $265^{\circ}$  C.) the first tinge of purple shows itself: this is the temper employed for pocket-knives;  $518^{\circ}$  ( $270^{\circ}$  C.) gives a purple, which is the tint for table and carving-knives. A temperature of from  $536^{\circ}$  to  $572^{\circ}$  ( $280^{\circ}$  to  $300^{\circ}$  C.) produces various shades of blue, such as are used for watch-springs, sword-blades, saws, and instruments requiring great elasticity. The different degrees of heat may be exactly regulated by heating the different articles in a fusible metal- or oil-bath, the temperature of which is ascertained by means of thermometers, though in ordinary cases this degree of nicety is not observed.

Hardened steel is somewhat less dense than wrought steel. It appears that a portion of the carbon contained in steel, before the alloy has been hardened, is in the uncombined state; this portion is left in the form of graphitic scales when the metal is dissolved in hydrochloric acid: but after the steel has been hardened, the whole of the carbon is chemically united with the iron; and when treated with acids, is left in the form of a liquid hydrocarbon. Before it has been hardened it may be worked as

easily as iron, and in certain cases may be welded upon that metal. Instruments are completely finished in the soft state, and are then hardened and subsequently tempered.

It is sometimes desirable to convert articles manufactured from soft iron superficially into steel. This is termed *case-hardening*, and is effected by heating them in contact with powdered cast-iron turnings, or sometimes with powdered charcoal. The same object is attained if they are sprinkled when red-hot, with powdered potassic ferrocyanide.

(752) *Preparation of pure Iron.*—In order to obtain iron chemically pure, Berzelius recommends that filings of the best bar iron be intimately mixed with one-fifth of their weight of pure ferric oxide, and placed in a Hessian crucible, covered with pounded glass (free from lead); the cover is then to be carefully luted on, and the crucible to be exposed for an hour to the strongest heat of a smith's forge. By this means, all traces of carbon and of silicon are oxidized at the expense of the oxygen of the ferric oxide, whilst the excess of oxide forms a fusible slag with the glass. If the operation be successful, the iron will be melted into a button, with a lustre approaching that of silver. Such iron is very tough, and much softer than ordinary bar iron: it has a sp. gr. of 7.8439. Pure iron may also be obtained in the state of fine powder, by decomposing the pure sesquioxide at a red heat in a current of hydrogen gas. Iron has been obtained in hollow tetrahedra, apparently belonging to the cubic system, by reducing ferrous chloride in a current of pure hydrogen. It may be deposited in flexible laminæ from a mixed solution of ferrous chloride and ammoniac chloride, by the action of the voltaic current.

(753) *Properties of Bar Iron.*—The bar iron of commerce is never pure. It always retains small quantities of carbon, varying from 0.2 to 0.4 per cent., and traces of silicon and sulphur; occasionally, also of phosphorus and arsenicum. The presence of this small quantity of carbon much increases its hardness and tenacity, but the other ingredients act injuriously upon the metal.

Bar iron has a bluish-white or grey colour, and is endowed with considerable lustre and hardness; it takes a high polish: its texture is usually fibrous, and when broken across it exhibits a ragged or hackly fracture; when rubbed, it emits a peculiar characteristic odour. The average specific gravity of good bar iron is 7.7. It requires the most intense heat of a wind furnace for its fusion. Iron passes through a soft pasty condition before it

is completely melted ; this property is one of great practical importance : if two pieces of iron be heated to whiteness, sprinkled with sand, and hammered together, they may be united or *welded* so completely, that the junction is as tough as any other part of the metal. The sand is used as a flux to the oxide of iron, with which it forms a slag which coats each piece of the metal ; by the blow of the hammer this layer of melted matter is forced out, and the two clean surfaces of metal become united together. At a red heat iron may be forged into any shape with facility, though at ordinary temperatures it possesses but little malleability, as compared with gold and silver. It however admits of being rolled into very thin sheets. In ductility, iron stands very high in the scale, and in tenacity it far exceeds all other known substances, with the exception of cobalt and nickel.

If compared with other metals, iron is inferior to many of them as a conductor of heat and of electricity. Its susceptibility to magnetism is peculiar ; no other metal exhibiting this property in any marked degree, excepting cobalt and nickel, and in them the power is developed to a much smaller extent. But though iron in its pure state is susceptible of magnetic induction, it cannot be permanently magnetized unless it be combined with carbon, as in steel ; with oxygen, as in the loadstone ( $\text{Fe}_3\text{O}_4$ ) ; or with sulphur, as in certain varieties of pyrites ( $\text{Fe}_3\text{S}_4$ ), and ( $\text{Fe}_7\text{S}_8$ ). It is especially worthy of observation, that if oxygen or sulphur be present in quantity either greater or less than in these particular compounds, not only is the power of retaining magnetism destroyed, but the mass becomes almost indifferent to the action of a magnet. Iron loses nearly all its magnetic power when heated to redness, but recovers it again on cooling.

At a high temperature iron burns readily, emitting vivid scintillations, as may be seen at the blacksmith's forge, or still more brilliantly when a glowing wire is introduced into a jar of oxygen. In a very finely divided state, such as that produced by reducing precipitated ferric oxide at a low temperature in a current of hydrogen gas, the metal takes fire by mere exposure to the atmosphere. If a small quantity of alumina be precipitated with the ferric oxide, so as to interpose some foreign matter between the particles of the metal, this pyrophoric property is much increased. A polished mass of the metal, however, preserves its lustre unchanged in dry air at ordinary temperatures for an unlimited time, but when exposed to a moist atmosphere, so that water in the liquid form shall be deposited upon the metal, its surface is quickly altered, and it becomes covered with rust.

When once a spot of rust begins to show itself, the oxidation proceeds rapidly : moisture is absorbed from the air by the oxide, and thus a species of voltaic action is produced, the oxide performing the part of an electronegative element, whilst the iron becomes electropositive, and the atmospheric moisture acts as the exciting liquid. The carbonic acid derived from the air contributes in an important way towards increasing the rapidity with which this change occurs ; but it is not indispensable. It appears that usually hydrated ferrous carbonate is first formed ; this is afterwards decomposed by the further absorption of oxygen by which it is converted into the hydrated sesquioxide, or rust of iron, whilst the liberated carbonic acid forms a fresh portion of ferrous carbonate : a portion of water is deoxidized in the process, and hydrogen is evolved ; if a considerable heap of iron turnings be moistened and exposed to air, the peculiar odour of hydrogen, as evolved from a metallic carbide, is perceived, and the temperature of the mass rises considerably. Iron rust always contains ammonia, derived probably from the reaction of the nascent hydrogen of the water upon the nitrogen of the atmosphere, which is dissolved in the water with which the metal is moistened. Even the native oxides of iron invariably contain traces of ammonia (Chevallier). Iron may be kept for any length of time without undergoing any change in water quite free from air, as well as in lime-water, or in water containing a little caustic or carbonated alkali, but the alkaline bicarbonates do not exert this protective action. At a red heat iron decomposes water rapidly, and liberates hydrogen (345), whilst the iron is converted into minute crystals of the black or magnetic oxide ; the following equation illustrates the chemical change :  $4\text{H}_2\text{O} + 3\text{Fe} = 4\text{H}_2 + \text{Fe}_3\text{O}_4$ .

Chlorine, bromine, and iodine combine quickly with iron, and dissolve it easily at ordinary temperatures, if the metal be digested with them in water. Iron is soluble in diluted sulphuric and hydrochloric acids, with extrication of hydrogen. Even carbonic acid, when contained in water from which air is excluded, slowly dissolves this metal with extrication of hydrogen, and the ferrous carbonate is dissolved in the excess of carbonic acid. Concentrated sulphuric acid has very little action on iron, even when boiled upon it—a slow solution, attended with the evolution of sulphurous anhydride, occurring : but the metal is rapidly attacked by nitric acid, with abundant evolution of nitric oxide.

(754) *Passive Condition of Iron.*—Under certain circumstances iron may be kept in concentrated nitric acid for weeks, without the slightest action, or

alteration of the polish of its surface. There are various methods of producing this *passive condition* of iron in an acid of a moderate degree of concentration; some of these seem to indicate an intimate connexion with its voltaic relations. This will be rendered evident from the following statement of some of the circumstances under which this remarkable phenomenon is manifested:—If a piece of clean iron wire be introduced into nitric acid of a sp. gr. of about 1·35, immediate and brisk action ensues; but if the metal be touched beneath the surface of the liquid with a piece of gold, of platinum, or of plumbago, the chemical action, contrary to what might have been anticipated, is suddenly arrested if the temperature of the acid has not been allowed to rise too high. If a second iron wire be made to touch the first, and then be introduced into the acid, it also is rendered inactive. This second wire may be used in like manner to render a third inactive. But if any of these inactive wires be withdrawn from the acid, and exposed to the air for a few seconds, it will be found to be rapidly acted on upon again introducing it into the acid. If whilst in the acid the iron wire be made the zincode of a voltaic arrangement, oxygen gas is evolved from the surface of the iron, but does not combine with it. If, on the contrary, a piece of passive iron be made the platinode or negative plate of the arrangement, it is immediately attacked by the acid.

By heating the end of a clean iron wire in the flame of a spirit-lamp so as to give it a superficial coating of oxide, the wire is brought into the passive condition.\* If into acid containing a passive wire, a second ordinary wire, not in contact with the first, be introduced, brisk action on the ordinary wire ensues; and on causing the passive wire to touch the active one, action immediately occurs on both.

Strong nitric acid, of sp. gr. 1·45, renders all iron passive; the metal may be kept in it for years without losing its brilliancy or showing any action; and a wire withdrawn from the strong acid and plunged into acid of 1·35, still remains passive. If it be wiped first, and then plunged into the weaker acid, it immediately begins to be dissolved. If the acid be diluted below a density of 1·35, it dissolves the metal rapidly, whatever may have been its previous condition.

*Silicide of Iron.*—Iron combines in various proportions with silicon, furnishing a brittle, white, fusible crystalline mass, which is but slowly attacked by hydrochloric acid. Hahn obtained a definite compound  $\text{Fe}_3\text{Si}_2$  of sp. gr. 6·611, containing 20·3 per cent. of silicon, by fusing at a prolonged high temperature ferrous sodio-chloride (obtained by fusing 40 parts of iron, 150 of sal ammoniac, and 80 of common salt) with a mixture of 5 parts of silicon, 25 of sodium, and 25 of fluor-spar.

It is probable that a compound of  $\text{SiFe}$  also exists, which would contain 33·3 per cent. of silicon.

(755) *Alloys of Iron.*—Iron forms alloys with most of the metals; but they are not in general of much importance. The presence of small quantities of silver, of copper, of arsenicum, or of sulphur, in iron, is said to occasion a defective quality of metal,

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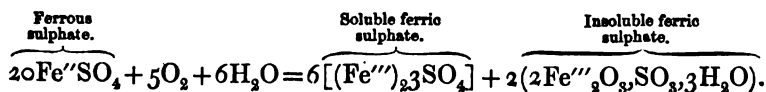
\* Similar effects are produced with wires of cobalt or of nickel, though with them the action is less strongly marked (Nicklès). Such wires, if placed in voltaic relation with an active wire of the same metal, are found to be strongly electronegative towards it; but passive iron, cobalt, and nickel are electropositive in relation to platinum. Andrews has shown that bismuth also may be rendered passive in concentrated nitric acid.

technically known as *red short*. Such iron is tough at ordinary temperatures, but becomes brittle when heated to redness for forging. The presence of a quantity of antimony not exceeding 0·23 per cent., was found by Karsten to render it both cold short and red short.

The mode of preparing zinc-plate or galvanized iron has been already described (707). Tin-plate is prepared by an analogous process; it consists of iron superficially alloyed with tin (811).

(756) OXIDES OF IRON.—Iron yields four definite compounds with oxygen: 1. The *protoxide* (FeO), which is the base of the green, or ferrous salts of iron: 2. The *sesquioxide* (Fe<sub>2</sub>O<sub>3</sub>), which is the base of the red, or ferric salts: 3. The black, or *magnetic oxide* (Fe<sub>3</sub>O<sub>4</sub>), which may be viewed as a compound of the two preceding oxides, or (FeO, Fe<sub>2</sub>O<sub>3</sub>); it does not form any definite salts: 4. *Ferric acid*, the anhydride of which is unknown; it is a weak and unstable metallic acid, and as such it reacts with the alkalies, forming salts like potassic ferrate K<sub>2</sub>FeO<sub>4</sub>.

FERROUS OXIDE; *Protoxide of iron* (FeO=72); *Comp. in 100 parts*, Fe, 77·78; O, 22·22.—It is obtained in the form of a white hydrate by dissolving a pure ferrous salt in water recently boiled, and precipitating it by an alkali the solution of which has been similarly treated, both being allowed to cool out of contact with air, and being mixed in vessels from which air is excluded. If this precipitate be boiled in a vessel from which oxygen is excluded, it loses its water of hydration, like cupric oxide under similar circumstances. Hydrated ferrous oxide absorbs oxygen greedily from the air, passing through various shades of light green, bluish green, and black, till finally it assumes an ochry hue, due to the formation of the hydrated sesquioxide. It is insoluble in water, but is somewhat soluble in ammonia; this solution quickly absorbs oxygen from the air, and a film of insoluble ferric oxide is formed upon its surface. Ferrous oxide is readily dissolved by acids, and forms with them salts which are known as the *ferrous salts* or *protosalts of iron*; they have a green colour, and an astringent, inky taste. The solutions of these salts, when exposed to the air, absorb oxygen gradually, and are decomposed; in which case ferric salts are formed, one portion of which is retained in solution, whilst a basic ferric salt falls as a rusty insoluble precipitate. For example, in the case of ferrous sulphate, the change may be represented as follows:—



(757) FERRIC OXIDE; *Peroxide*, *Red oxide*, or *Sesquioxide of iron* ( $\text{Fe}'''_2\text{O}_3 = 160$ ); *Comp. in 100 parts*, Fe, 70; O, 30.—The anhydrous sesquioxide is obtained for the arts by igniting the ferrous sulphate (767), and is known under the names of *colcothar*, *crocus of Mars*, or *rouge*, according to the degree of levigation to which it has been submitted; it is extensively employed, amongst other uses, for polishing glass, and by jewellers for putting a finish to their goods. It is also employed as a red pigment.

The sesquioxide occurs native in great abundance: several of its varieties have been already mentioned as among the most valuable ores of iron. The specular ore of Elba (sp. gr. 5.22) often presents natural facets of the most perfect polish, and of remarkable size and lustre. It occurs crystallized in forms of the rhombohedral system, and is isomorphous with alumina in corundum. Red hæmatite, or *bloodstone* (sp. gr. from 4.8 to 5.0), another of its varieties, is extremely hard, and, when polished, is employed for burnishing gilt trinkets.

\* *Hydrates of Ferric Oxide.*—There are several of these. Brown hæmatite is the hydrate ( $2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}$ ) sp. gr. 3.98. This mineral is readily dissolved by acids. It contains 59.89 per cent. of iron, with 25.67 of oxygen, and 14.44 of water. Another native hydrate, *göthite* ( $\text{H}_2\text{O}, \text{Fe}_2\text{O}_3$ ; sp. gr. 4.12 to 4.37) has been found crystallized in prisms. Brown hæmatite gives the red and yellow colour to the different varieties of clay.

The sesquioxide is best obtained in a state of purity, by precipitating the ferric chloride by ammonia in excess. It falls as a bulky light-brown flocculent hydrate, which shrinks remarkably as it dries: if precipitated in a cold solution, and dried without heat over sulphuric acid, it contains  $2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}$  (St. Gilles), but it is apt to retain a little ammonia, which is easily expelled by heat. The same hydrate is also formed when moist iron is allowed to become oxidized by exposure to air. If the hydrate be not dried, but allowed to remain for some months under water, it becomes crystalline, and according to Wittstein, is converted into an allotropic hydrate ( $2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O} ?$ ), but if dried at  $100^\circ \text{C}$ . it retains 10.11 per cent. of water, corresponding in composition to  $(\text{Fe}_2\text{O}_3, \text{H}_2\text{O})$ . Hydrated ferric oxide slowly parts with its water at a prolonged heat of  $608^\circ$  ( $320^\circ \text{C}$ .), and if subsequently heated to dull redness, it suddenly contracts in bulk, and glows brightly for a few moments whilst undergoing molecular change; after this it is dissolved by acids with difficulty, but is more readily attacked by a solution of ferrous chloride in hydrochloric acid: at a very high temperature the sesquioxide loses one-ninth of its oxygen, and is converted into the magnetic oxide of iron.

Hydrated ferric oxide, when recently precipitated from cold solutions, is easily soluble in acids, forming the *persalts of iron*, or *ferric salts*; they have a strongly acid reaction, and do not crystallize: many of them are deliquescent. Their concentrated



solutions have the property of dissolving a considerable excess of the oxide, in which case they assume a deep red colour. If these basic solutions be diluted and boiled, the iron is entirely separated in the form of an insoluble ferric subsalt.

If well washed and freshly precipitated hydrated ferric oxide, obtained by the action of ammonia upon ferric chloride in the cold, be boiled in water for a few minutes, it becomes converted into the hydrate,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; but if the ebullition be continued for 8 or 10 hours, its colour becomes changed from ochry brown to brick red, and it is converted into an allotropic modification of the same hydrate, and by prolonged boiling a portion of it even loses all its water. This modified oxide is insoluble in strong boiling nitric acid, and only slowly soluble in hot hydrochloric acid. Cold acetic acid, and cold diluted hydrochloric and nitric acids dissolve it, forming a red liquid which appears to be turbid by reflected light; concentrated nitric or hydrochloric acid occasions a red precipitate in this solution, but it becomes redissolved on the addition of water. The solution is also precipitated by the addition of any sulphate, or of any salts of the alkali-metals. If the ordinary hydrated ferric oxide be kept long in water, especially if at the same time it be exposed to a low temperature, it experiences a similar modification in composition and properties. An acetic solution of this oxide, if kept for some time in a closed vessel at  $100^\circ \text{C}$ ., becomes of a brighter red colour. It appears to be turbid when viewed by reflected light, but clear by transmitted light. It has lost its astringent metallic taste. The addition of a soluble sulphate causes an immediate precipitate, and so do the strong acids: it is no longer reddened by the addition of a sulphocyanide, and does not give a precipitate of Prussian blue with potassic ferrocyanide (Péan de St. Gilles, *Ann. de Chimie*, III. xlv. 47). Graham found that if a solution of ferric chloride, in which a large quantity of hydrated ferric oxide had been dissolved by prolonged digestion in the cold, were submitted to dialysis, a solution was eventually obtained which contained a proportion of 98.5 of the oxide and 1.5 of hydrochloric acid. This solution, however, in a few weeks became gelatinous spontaneously in the bottle to which it was transferred.

Hydrated ferric oxide is now used to some extent for the purpose of purifying coal-gas from sulphuretted hydrogen, which is always produced during the distillation of coal. For this purpose the oxide is mixed with sawdust, and placed, in layers of 10 or 12 inches (25 or 30 cm.) in thickness, upon the perforated shelves of a dry lime purifier: hydrated ferric sesquisulphide and water are formed;  $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O} + 3\text{H}_2\text{S} = \text{Fe}_2\text{S}_3 \cdot x \text{H}_2\text{O} + 3\text{H}_2\text{O}$ . After the mixture has ceased to absorb any more sulphuretted hydrogen, it is oxidized by exposure to a current of air; hydrated ferric oxide is thus reproduced, and sulphur is set free;  $2\text{Fe}_2\text{S}_3 \cdot x \text{H}_2\text{O} + 3\text{O}_2 = 2\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O} + 3\text{S}_2$ . The mixture may again be used for the same purpose as at first, and this process may be repeated several times in succession, until the accumulation of sulphur mechanically impairs the absorbent powers of the mixture. Considerable elevation of temperature attends the act of reoxidation, which must therefore be prevented from taking place with too much rapidity.

Ferric oxide combines with some of the more powerful bases, towards which it acts the part of a feeble acid. The compounds which it forms by heating it with the potassic and sodic hydrates are easily decomposed by water, but the oxide retains traces of these bases with great obstinacy. According to Pelouze, when 4 atoms of lime and 1 atom of ferric oxide are precipitated together and boiled, they unite and form a white compound ( $4\text{CaO}, \text{Fe}_2\text{O}_3$ ) which is readily decomposed by the feeblest acids. Ferric oxide occurs native combined with zincic oxide in crystals, mixed with oxide of manganese, constituting *Franklinite*. With ferrous oxide it forms the black or magnetic oxide of iron.

(758) *Black or Magnetic oxide of iron* ( $\text{Fe}_3\text{O}_4$ ); *Sp. Gr.* 5.09; *Comp. in 100 parts*, Fe, 72.41; O, 27.59.—This oxide occurs as a well-known mineral, the *loadstone*, which acquires its magnetism from the inductive influence of the earth. It is found in primitive rocks, forming beds, or sometimes, as in Sweden, entire mountains. It furnishes a very pure and excellent iron, of which a large quantity is annually supplied from the Swedish and American mines. It has a black colour and metallic lustre; it crystallizes in cubes, octohedra, or rhombic dodecahedra. Magnetic oxide of iron is the principal constituent of the scales of oxide which are detached during the forging of wrought iron. It fuses at a high temperature, and is formed when iron is burned in oxygen,—the sesquioxide, which is the result of the combination, losing part of its oxygen, owing to the intensity of the heat developed during the combustion. The magnetic oxide is also formed by passing steam over heated iron turnings. A hydrate of this oxide ( $\text{Fe}_3\text{O}_4, \text{H}_2\text{O}$ ) may be procured by dividing a freshly prepared solution of ferrous sulphate into three equal portions: two of these are acidulated with sulphuric acid and heated to the boiling-point; to the boiling liquid nitric acid is added gradually so long as its addition causes the evolution of nitric oxide: when this point is reached, the whole of the ferrous salt will have been converted into a ferric salt;  $6 \text{Fe}''\text{SO}_4 + 3 \text{H}_2\text{SO}_4 + 2 \text{HNO}_3 = 3 (\text{Fe}''', 3 \text{SO}_4) + 2 \text{NO} + 4 \text{H}_2\text{O}$ : the remaining portion of the solution of the ferrous sulphate is then poured into the hot liquid, and sodic carbonate or caustic ammonia is added in slight excess: the solution and precipitate are boiled together, and the black oxide is formed as a heavy crystalline powder. The magnetic oxide is soluble without difficulty in hydrochloric acid, as well as in nitric acid and in aqua regia: this oxide, however, when treated with acids does not form specific salts, but mixtures of ferrous and ferric salts; for example,  $\text{Fe}_3\text{O}_4 + 4 \text{H}_2\text{SO}_4 = \text{Fe}''\text{SO}_4 + \text{Fe}'''_2\text{SO}_4 + 4 \text{H}_2\text{O}$ .

If recently precipitated hydrated ferric oxide, obtained from ferric chloride by ammonia, be well washed, and without being dried be boiled with water and iron turnings in large excess, hydrogen is evolved, and magnetic oxide of iron formed.

(759) *Ferric acid* ( $\text{H}_2\text{FeO}_4 = 122$ ).—If a mixture of 1 part of ferric oxide and 4 parts of nitre be heated to full redness for some time, a brown mass is obtained, which with water gives a beautiful violet-coloured solution, due to the presence of potassic ferrate. In this compound the iron is combined with a larger quantity of oxygen than in the sesquioxide, but the ferric anhydride has not been obtained in an isolated form. Potassic ferrate may be more easily procured by suspending 1 part of recently precipitated hydrated ferric oxide in a concentrated solution of potash, consisting of 30 parts of potassic hydrate and 50 of water, and then transmitting a current of chlorine gas: the potassic ferrate is insoluble in a concentrated solution of potash, and is deposited as a black powder, which may be drained upon a tile (Fremy). This compound is very soluble in water, but is precipitated in black flocculi by a large excess of alkali. It is a very unstable salt: in dilute solutions the alkali becomes free, hydrated ferric oxide subsides, and oxygen escapes. Organic matter decomposes it speedily, just as it does the potassic permanganate: a temperature of  $100^\circ\text{C}$ . destroys it instantly if in solution, and the addition of an acid, even in quantity insufficient to neutralize the whole of the alkali, causes the immediate separation of oxygen, and precipitation of ferric oxide.

Baric, strontic, and calcic ferrates may be obtained in the form of red insoluble precipitates, by admixture of solutions of the salts of the earths with a solution of potassic ferrate.

*Hydride of Iron*.—Wanklyn and Carius have described a compound of hydrogen with iron procured by the action of ferrous iodide on zinc-ethyl. It has not been analysed, but is described as a black powder which evolves pure hydrogen when gently heated: hydrochloric acid dissolves it with evolution of hydrogen.

(760) *Nitrides of Iron*.—When iron wire is heated in a current of dry ammoniacal gas for some hours it becomes brittle, but does not usually gain in weight more than about 0.2 per cent. Despretz, however, obtained a compound of iron with nitrogen in which 100 parts of iron increased to 111.5, becoming less dense, brittle, whitish, and less oxidizable than pure iron. Sulphuric acid dissolves this nitride easily with evolution both of hydrogen and nitrogen, whilst ammoniac sulphate is retained in solution. If heated to redness in a current of dry hydrogen it becomes reduced to metallic iron, whilst ammonia is generated. Fremy states that it becomes easily and permanently magnetized. He found the best mode of preparing this nitride, to which he attributes a composition expressed by the formula ( $\text{Fe}_2\text{N}_3$ ), to consist in transmitting a current of dry ammonia over dried ferrous chloride heated to low redness in a porcelain tube. Stahlschmidt thus obtained the compound  $\text{Fe}_2\text{N}$ . If pure ferric oxide, as obtained from the oxalate by ignition, be heated in a current of ammonia, a brittle nitride is formed, consisting of  $\text{Fe}_3\text{N}$  (Rogostadius).

(761) **SULPHIDES OF IRON**.—Sulphur combines with iron in several proportions: the protosulphide,  $\text{FeS}$ , and the disulphide,  $\text{FeS}_2$ , are the most important; but besides these a subsulphide,  $\text{Fe}_2\text{S}$ , has been obtained by heating ferrous sulphate to redness in a current of hydrogen gas: a sesquisulphide,  $\text{Fe}_2\text{S}_3$ , may also be formed as a hydrate by precipitating the ferric salts by the protosulphides of the alkali-metals; and two magnetic sulphides of iron,  $\text{Fe}_7\text{S}_8$ , and  $\text{Fe}_3\text{S}_4$ , are found native.

*Ferrous Sulphide, Protosulphide or Sulphuret of iron* ( $\text{FeS} = 88$ ), may be prepared by heating a bar of iron to whiteness and bringing it into contact with a roll of sulphur: immediate union

takes place, and the resulting sulphide melts and runs down in drops of a reddish-brown colour: when formed in this manner it usually contains an excess of sulphur. It may also be prepared by projecting in successive portions, into a red-hot earthen crucible, a mixture of 7 parts of iron filings with 4 parts of sulphur in fine powder; vivid deflagration occurs at the moment of combination. Ferrous sulphide dissolves both iron and sulphur if either be present in excess; its composition, therefore, is variable. Like carbon, the presence even of a minute portion of sulphur alters the quality of wrought iron, which if it contains even  $\frac{1}{10,000}$  of sulphur is rendered 'red short.' Anhydrous ferrous sulphide is dissolved by diluted sulphuric or hydrochloric acid with evolution of sulphuretted hydrogen: this decomposition is frequently employed in the laboratory as a convenient source of sulphuretted hydrogen. Nitric acid and aqua regia decompose it and form ferric nitrate or ferric chloride, setting part of the sulphur free, and converting the residue into sulphuric acid. When heated in the open air, this sulphide absorbs oxygen and becomes converted into ferrous sulphate; at a still higher temperature it is decomposed, sulphurous and sulphuric anhydrides escape, and ferric oxide remains.

Ferrous sulphide may be obtained as a black hydrate by precipitating a solution of a ferrous salt with a solution of a hydrosulphide of one of the alkali-metals; thus  $2\text{KHS} + \text{FeSO}_4 + x\text{H}_2\text{O} = \text{FeS}x\text{H}_2\text{O} + \text{H}_2\text{S} + \text{K}_2\text{SO}_4$ ; in this condition it rapidly attracts oxygen from the air, and assumes a brownish-red colour, ferric oxide being formed and sulphur liberated. When iron is present in very minute quantities in a solution, and is precipitated by a solution of ammoniac hydrosulphide, the very finely divided particles of ferrous sulphide are apt to pass through the filter; the liquid then has a peculiar green tint.

If iron filings be mixed with two-thirds of their weight of sulphur in powder, and moistened, the mixture becomes hot when exposed to the air, and absorbs oxygen with sufficient rapidity to cause it in many cases to inflame; ferrous sulphide is at first formed, and this quickly becomes converted into sulphate. A valuable lute for the joints of iron vessels is composed of a mixture of 60 parts of iron filings sifted fine, and 2 of sal ammoniac in fine powder intimately blended with 1 part of flowers of sulphur. This powder is made into a paste with water, and applied immediately; in a few minutes it becomes hot, swells, disengages ammonia and sulphuretted hydrogen, and soon sets as hard as iron itself.

(762) *Ferric disulphide, or Bisulphide of iron* ( $\text{FeS}_2 = 120$ ); *Sp. Gr.* 4.98; *Comp. in 100 parts*, Fe, 46.67; S, 53.33.—This compound is found abundantly in the native state, constituting the *iron pyrites* of mineralogists. It occurs in the strata of every

period: when found in the older formations it is crystallized in cubes, and sometimes in dodecahedra, of a brassy lustre, and is hard enough to strike fire with steel; but in the tertiary strata it occurs more frequently in fibrous radiated nodules. The formation of iron pyrites may occasionally be traced to the slow de-oxidation of sulphates by organic matter in waters containing carbonate or other salts of iron in solution; it is then frequently deposited in cubes or octohedra. This appears to be the usual mode of its formation in alluvial soils. Some varieties of iron pyrites, especially those found in the tertiary strata, are speedily decomposed by exposure to air; oxygen is absorbed, and ferrous sulphate formed. This decomposition occurs with greater facility if the disulphide be mixed with other substances, as is the case in the aluminous schists; in which, by the further action of air, a basic ferric sulphate is formed, whilst the liberated sulphuric acid reacts upon the alumina, magnesia, or lime of the soil, and forms sulphates; those of aluminum and magnesium may be extracted by lixiviation. The ordinary crystallized pyrites from the older strata is not thus decomposed, but a variety of a whiter colour is disintegrated rapidly by exposure to the weather; this form of pyrites is known as *marcasite*, or *white iron pyrites*; it crystallizes in right rhomboidal prisms, but it possesses the same chemical composition as the yellow cubes.

Iron pyrites is not acted upon by cold sulphuric or by hydrochloric acid, but is rapidly oxidized and dissolved by nitric acid and by aqua regia: boiling oil of vitriol dissolves it gradually with evolution of sulphurous anhydride. When heated in closed vessels it fuses, and sulphur is expelled. If heated in the air it burns with flame, ferric oxide is formed, whilst sulphurous anhydride escapes in large quantity. This circumstance has been turned to account in the manufacture of oil of vitriol, for which purpose enormous quantities of *mundic*, as the disulphide is termed by the workmen, are annually consumed. The acid obtained from that source is usually contaminated with arsenic, which in small quantity is a common impurity in pyrites. Iron pyrites may be prepared artificially by exposing a mixture of powdered ferrous sulphide with half its weight of flowers of sulphur, in a covered crucible to a heat just below redness, as long as sulphurous fumes escape.

(763) *Magnetic sulphide of Iron* ( $\text{Fe}_3\text{S}_4$ ); *Sp. Gr.* 4.65.—This compound exhibits a brassy lustre, but is distinguished from ordinary pyrites by its solubility in hydrochloric acid. It is often formed when sulphur and iron are heated together in preparing ferrous sulphide for use in the laboratory. Another variety of magnetic pyrites consists of  $\text{Fe}_3\text{S}_4$ .

*Mispickel*, or arsenical pyrites, is an arsenio-sulphide of iron ( $\text{FeSAs}$ ; *Sp. Gr.* 6.13) which, amongst other localities, occurs abundantly in the Hartz, in Saxony, and in some of the Cornish mines; it crystallizes in right rhombic prisms, of a steel-grey colour and metallic lustre. When heated in closed vessels it is partially decomposed, and arsenious sulphide sublimes. If exposed to a high temperature in the open air, it produces ferric oxide, whilst arsenious and sulphurous anhydrides escape. Analogous compounds of cobalt and nickel occur amongst the ores of these metals.

A remarkable class of compounds, termed by Roussin, who discovered them, *nitrosulphides of iron*, may be obtained by the reaction of potassic nitrite and hydro-ammonic sulphide upon the salts of iron. The reaction is complicated, and their properties will be better examined along with those of the nitro-prussides.

*Diferrous phosphide* ( $\text{Fe}_2\text{P}$ ) may be obtained by reducing the phosphate of the metal with charcoal: it fuses at a red heat, and forms an extremely hard, brittle mass, which unites with both phosphorus and iron in all proportions: its presence even in small proportion in bar iron appears to produce metal of the defective quality known as *cold short* iron.

(764) **CHLORIDES OF IRON.**—Iron forms with chlorine two compounds—ferrous chloride,  $\text{FeCl}_2$  and ferric chloride,  $\text{Fe}_2\text{Cl}_6$ ,—which correspond in composition to the two basic oxides of the metal.

*Ferrous Chloride, Protochloride of Iron*, ( $\text{FeCl}_2=127$ ); *Sp. Gr. anhydrous*, 2.528.—By passing dry hydrochloric acid gas over ignited metallic iron, the acid is decomposed, hydrogen gas escapes, chlorine combines with the iron, and the white anhydrous ferrous chloride sublimes at a temperature at which glass begins to soften. Its solution may be formed by dissolving iron in hydrochloric acid; the hot, saturated liquid deposits the salt, on cooling, in green hydrated crystals ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ; *Sp. Gr.* 1.926). It is very soluble in water, and is taken up in considerable quantity by alcohol. If heated in the open air, chlorine escapes and ferric oxide remains.

Ferrous chloride unites with ammoniac chloride, and forms a double salt, from which the iron may be deposited upon various metallic articles, by boiling them in this solution with scraps of zinc; the zinc displaces the iron, which is deposited in a coherent lamina upon the other metals, in consequence of a voltaic action.

(765) *Ferric Chloride, Sesquichloride or Perchloride of iron* ( $\text{Fe}_2\text{Cl}_6=325$ ); *Sp. Gr. of Vapour*, 11.39; *Mol. Vol.*  $\square$ ; *Rel. wt.* 162.5.—This compound sublimes in anhydrous brown scales when dry chlorine gas is transmitted over iron heated to redness.

The anhydrous chloride is very deliquescent, and hisses when thrown into water, forming a red solution. It is also soluble both in alcohol and ether. In a hydrated condition it may be procured by evaporating a solution of ferrous chloride through which chlorine has been passed to saturation, or by dissolving hydrated ferric oxide in hydrochloric acid: the solution, by concentration, yields large, red deliquescent crystals ( $\text{Fe}_2\text{Cl}_6 \cdot 6\text{H}_2\text{O}$ ), but the salt cannot be rendered anhydrous by evaporation, as it is decomposed into hydrochloric acid and ferric oxide. It also crystallizes in stellate, orange-coloured groups, with  $12\text{H}_2\text{O}$ , which are less deliquescent than the other hydrate. Crude ferric chloride is sometimes used in solution as a disinfectant: it deodorizes sewerage products quickly, and is partially reduced to the condition of ferrous chloride. Ferric chloride forms a double salt with ammoniac chloride, which crystallizes readily in cubes, and is known in pharmacy as the *ammonio-chloride of iron*. The composition of this salt varies considerably: it is of a ruby-red colour, and seldom contains more than 2 per cent. of iron. A double salt of ferric chloride with sodic chloride and with potassic chloride may also be formed.

A hydrated *ferric oxychloride* is formed when a solution of ferrous chloride is exposed to the air, or when ferric chloride is precipitated by a small quantity of caustic alkali. It is insoluble in water containing salts, but is partially soluble in pure water.

(766) The BROMIDES of iron correspond in composition to the chlorides.

*Ferrous iodide*, or *Protiodide of iron* ( $\text{FeI}_2 = 310$ ), is formed by digesting iron wire or filings, in a closed vessel, with four times their weight of iodine suspended in water: direct combination takes place between the elements, the iodide is dissolved and forms a pale-green solution, which, by evaporation *in vacuo*, yields crystals containing  $\text{FeI}_2 \cdot 4\text{H}_2\text{O}$ ; sp. gr. 2.873. By a continued heat it may be rendered anhydrous, and in that state is fusible. Its solution, if exposed to the air, absorbs oxygen and is decomposed: iodine is set free, and a hydrated ferric oxyiodide falls. This change is retarded by mixing the solution with strong syrup; and as the compound is employed in medicine, this method is frequently adopted to preserve uniformity in its composition. No definite *ferric iodide* is crystallizable.

(767) FERROUS SULPHATE, *Protosulphate of iron*, *Copperas*, or *Green vitriol* ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 152 + 126$ ); *Sp. Gr. anhydrous*, 3.138, *cryst.* 1.857; *Comp. cryst. in 100 parts*,  $\text{FeO}$ , 25.91;  $\text{SO}_3$ , 28.77;  $\text{H}_2\text{O}$ , 45.32.—This salt is prepared in a state of purity by dis-

solving 1 part of pure iron, or  $1\frac{1}{2}$  of ferrous sulphide, by the aid of heat, in  $1\frac{1}{2}$  part of oil of vitriol diluted with 4 of water. On filtering the solution quickly, it deposits beautiful transparent, bluish-green, rhomboidal crystals on cooling, with  $7\text{H}_2\text{O}$ . They effloresce in a dry air, and form a white crust, which soon becomes of a rusty-brown colour, owing to the absorption of oxygen and formation of a basic ferric sulphate. If crystallized at a temperature of  $176^\circ$  ( $80^\circ\text{C.}$ ) the ferrous sulphate forms right rhombic prisms, which contain only  $4\text{H}_2\text{O}$ . It may also be obtained crystallized with 3 and with 2 atoms of water. For commercial purposes ferrous sulphate is formed by the decomposition of iron pyrites, or of aluminous schists containing pyrites, as already described when speaking of the manufacture of alum (667). The ferrous sulphate thus obtained has a grass-green colour, owing to the presence of a little ferric sulphate. Ferrous sulphate is largely used in combination with astringent vegetable matters as a black dye; ordinary writing-ink is a compound of this kind.

This salt is insoluble in alcohol, and requires twice its weight of cold water for its solution. Its solubility is greater at  $194^\circ$  ( $90^\circ\text{C.}$ ) than at  $212^\circ$  ( $100^\circ\text{C.}$ ), 100 parts of water dissolving 370 parts of the crystals at  $90^\circ\text{C.}$  and only 333 at the boiling-point. This anomaly is probably dependent upon causes similar to those observed in the case of the sodic sulphate and carbonate. If exposed to the air, the solution absorbs oxygen, and a rusty precipitate occurs, which is a basic ferric sulphate composed of  $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$ , while normal ferric sulphate remains in solution. Owing to its strong attraction for oxygen, ferrous sulphate is occasionally used as a reducing agent: it is thus employed to precipitate gold and palladium in the metallic form from their solutions, and indigo is by its means brought into the soluble condition. If heated gradually, each atom of the crystallized sulphate loses 6 atoms of water and forms a white powder; 1 atom of water being retained at all temperatures below  $500^\circ$  ( $260^\circ\text{C.}$ ) At a red heat the sulphate is decomposed; sulphuric anhydride is liberated, but one portion of the anhydride yields part of its oxygen to the iron, which is converted into the sesquioxide, whilst sulphurous anhydride escapes ( $2\text{FeSO}_4 = \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$ ); but as in practice the salt cannot be rendered anhydrous in large quantities, a little water distils with the sulphuric anhydride, which is condensed as a brown fuming liquid, the 'Nordhausen sulphuric acid' (415). The residual ferric oxide is sold under the name of colcothar (757).



The aqueous solution of ferrous sulphate, in common with that of all the ferrous salts, has the power of absorbing a large quantity of nitric oxide; forming a deep brown solution which has a strong attraction for oxygen: if this solution be heated in closed vessels, the gas is for the most part expelled unchanged; if heated in air, nitric acid is formed in the liquid, and this converts the iron into a ferric salt.

With the sulphates of potassium and ammonium, green vitriol yields double salts precisely analogous in form and composition to those which are formed by these sulphates with cupric sulphate. The formula of the potassic salt is  $(\text{FeSO}_4, \text{K}_2\text{SO}_4, 6\text{H}_2\text{O})$ .

(768) *Ferric sulphate; Persulphate or Sesquisulphate of iron* ( $\text{Fe}'''_2\text{SO}_4 = 400$ ), is made either by treating brown hæmatite with an excess of strong sulphuric acid, allowing it to digest for some time, and then expelling the excess of acid at a heat short of redness; or by adding to the solution of 1 equivalent of ferrous sulphate, half an equivalent of oil of vitriol, boiling, and peroxidizing the iron by adding to the solution nitric acid in small quantities as long as any red fumes are given off. A yellowish-white deliquescent mass is obtained on evaporation, from which the acid is expelled by a red heat; at a more moderate heat the salt is rendered anhydrous: water dissolves it but slowly. It is found native in large quantities in Chili as *coquimbite*, in the form of a white silky crystalline mineral, or of a white powder ( $\text{Fe}'''_2\text{SO}_4, 9\text{H}_2\text{O}$ ). Several hydrated basic ferric sulphates may be obtained.

With potassic sulphate and the sulphates of the other alkali-metals ferric sulphate forms double salts, resembling common alum, in form and composition as well as in taste. The potassic salt ( $\text{KFe}'''_2\text{SO}_4, 12\text{H}_2\text{O}$ ) is astringent, very soluble in water, but insoluble in alcohol: it is very prone to spontaneous decomposition, and becomes converted from a colourless transparent crystal into a brown, gummy, deliquescent mass: this change is also produced by heating the salt to a temperature below  $100^\circ \text{C}$ . The mixed solutions of the two sulphates should therefore be allowed to evaporate spontaneously during the preparation of this salt. The double salt with ammonium ( $\text{H}_4\text{NFe}'''_2\text{SO}_4, 12\text{H}_2\text{O}$ , *sp. gr.* 1.718) is much more permanent, and crystallizes readily in beautiful octohedra.

(769) **FERROUS NITRATE** ( $\text{Fe}_2\text{NO}_3, 6\text{H}_2\text{O} = 180 + 108$ ).—This salt may be obtained by dissolving ferrous sulphide in cold nitric acid diluted with 4 or 5 times its bulk of water. Sulphuretted hydrogen is evolved in abundance, and on evaporating the solution *in vacuo* over oil of vitriol, it crystallizes in pale-green rhombohedra, which when heated evolve nitric oxide, and yield a basic ferric



nitrate;  $6(\text{Fe}_2\text{NO}_3) = 2\text{NO} + 3\text{Fe}_2\text{O}_3, 5\text{N}_2\text{O}_5$ . This change sometimes occurs in warm weather spontaneously. The basic salt is then freely soluble in water, and is not decomposed by ebullition. Ferrous nitrate may also be procured by decomposing a solution of ferrous sulphate by an equivalent quantity of baric nitrate. It cannot be obtained in a pure form by treating iron with diluted nitric acid: since in that case the metal is dissolved without evolution of gas, and ammonia is formed in the liquid;  $10\text{HNO}_3 + 4\text{Fe} = 4(\text{Fe}_2\text{NO}_3) + \text{H}_4\text{NNO}_3 + 3\text{H}_2\text{O}$ .

*Ferric Nitrate* ( $\text{Fe}'''_3\text{NO}_3, x\text{H}_2\text{O}$ ).—When nitric acid of sp. gr. 1·2 or 1·3 is digested upon metallic iron, a violent action occurs attended with the extrication of nitrous anhydride and of nitric oxide; the iron is at the same time converted into ferric nitrate, which is obtained with difficulty on evaporation in prismatic hydrated crystals. An insoluble basic nitrate is commonly formed at the same time.

(770) **FERROUS CARBONATE** or *Protocarbonate of iron* ( $\text{FeCO}_3 = 116$ ; *Comp. in 100 parts*, Fe, 48·27, or FeO, 62·07;  $\text{CO}_2$ , 37·93.—This substance is found native in immense quantities, forming a valuable ore of iron. In its less usual condition, when crystallized, it constitutes spathic iron ore, and occurs in yellowish lenticular crystals, the primary form of which is a rhombohedron, isomorphous with calcareous spar. The native carbonate very often contains manganous carbonate. The clay-iron ore, from which the greater part of the English iron is obtained, is, as already mentioned, an impure ferrous carbonate. Clay iron-stone, besides the more usual form of bands or seams accompanying the coal strata, occurs also in detached nodules or lumps, sometimes of very large size, imbedded in the clay of the same formations. When ferrous carbonate is heated strongly in vessels from which air is excluded, carbonic anhydride and carbonic oxide are expelled, and magnetic oxide of iron is left, the decomposition being as follows:  $3\text{FeCO}_3 = \text{Fe}_3\text{O}_4 + 2\text{CO}_2 + \text{CO}$ . Ferrous carbonate is the salt contained in most ferruginous springs, in which it is held in solution by free carbonic acid: it is rarely present in a larger quantity than 1 grain per pint. Mere exposure to air causes its separation; the acid escapes, oxygen is absorbed, and hydrated ferric oxide, mixed with a small quantity of organic matter, subsides, forming the ochry deposits so usual around chalybeate springs. Ferrous carbonate may be produced artificially by mixing a ferrous salt with a carbonate of one of the alkali-metals, when it falls as a pale green voluminous hydrate which is speedily altered by exposure to air; it absorbs oxygen, rapidly losing its carbonic acid, and is converted into the red hydrated sesquioxide; during the process of drying it is therefore almost completely decomposed. No stable ferric carbonate exists, but the hydro-potassic and the hydrosodic carbonate dissolve the hydrated ferric

oxide; the red solution thus formed is very slowly decomposed by prolonged ebullition.

(771) **OXALATES OF IRON.**—*Ferrous oxalate* ( $2\text{FeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ ) is occasionally formed in the brown-coal strata, in yellow fibrous or granular masses, known as *Humboldtite* or *iron-resin*. It may be prepared artificially by precipitating the solution of ferrous sulphate by ammoniacal oxalate; or by exposing a solution of ferric oxalate in oxalic acid to the sun. Carbonic acid is then evolved, and ferrous oxalate with  $2\text{H}_2\text{O}$  is thrown down as a yellow crystalline and nearly insoluble powder.

*Ferric oxalate* is also a lemon-yellow powder, nearly insoluble in water, but soluble in excess of oxalic acid. It may be obtained by mixing a slight excess of a ferric salt with one of a soluble oxalate.

Ferric oxalate forms several double salts of the formula  $(\text{M}_2\text{Fe}'''_2\text{C}_2\text{O}_4)_x$ , analogous to the blue double oxalates of chromium (794). Double ferric oxalates with potassium, sodium, ammonium, barium, strontium, and calcium have been obtained by digesting the acid oxalates of these metals upon hydrated ferric oxide. These double oxalates are all freely soluble. It is owing to the formation of the soluble potassium salt that hydropotassic oxalate (salt of sorrel) is useful for removing stains of ink and of ferric oxide from linen.

(772) **PHOSPHATES OF IRON.**—*Ferrous hydric phosphate* ( $\text{Fe}''\text{HPO}_4$ ) falls as a white powder on adding trisodic phosphate to a ferrous salt; by exposure to air it absorbs oxygen, and becomes blue. A hydrated blue phosphate of iron is found native; it is known as *vivianite*. It is probably a mixture of ferrous and ferric phosphates ( $\text{Fe}''\text{HPO}_4 \cdot 2\text{Fe}'''\text{PO}_4$ ), and contains in addition  $8\text{H}_2\text{O}$ , or about 30 per cent. of water.

A *ferric phosphate* ( $\text{Fe}'''\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ) is obtained as a white powder by decomposing ferric chloride by an alkaline orthophosphate. Exposure of this salt to air produces no change. It is insoluble in acetic acid, but soluble in ferric acetate: phosphoric acid is sometimes precipitated in this form in the course of analysis. Its composition varies according as the sodic phosphate or the ferric salt is in excess.

Several native *silicates of iron* are known, but they are not important. The 'finery slag' obtained in the conversion of cast into wrought iron consists chiefly of ferrous orthosilicate ( $2\text{FeO} \cdot \text{SiO}_2$ ). Oxide of iron rapidly attacks clay crucibles if fused in them.

(773) **CHARACTERS OF THE SALTS OF IRON.**—Iron forms two classes of salts, both of which are readily distinguished from each other and from those of other metals. The salts of iron are not poisonous, unless administered in excessive quantities; they form valuable tonics and astringents when taken internally. The solutions both of the ferrous and of the ferric salts have an inky, astringent taste.

1. *Ferrous salts, or Salts of the protoxide.*—These salts, when in solution, or when crystallized, have a pale-green colour; they redden litmus, but very feebly. With the *alkalies* a grey or green precipitate of hydrated protoxide is formed in their solutions: it passes quickly through various shades of green into brown by

exposure to the air; this change of colour is due to the absorption of oxygen, in consequence of which the sesquioxide is eventually obtained. If the precipitate be produced by *ammonia*, an excess of this reagent redissolves a part of the precipitate; and if the solution contains ammoniac chloride, the whole of the oxide will be redissolved: this solution absorbs oxygen rapidly from the air, and a film of ferric oxide is formed upon the surface. Ferrous salts of the mineral acids are not precipitated in slightly acid solutions by *sulphuretted hydrogen*; but they give a black precipitate of hydrated sulphide on adding a solution of *ammonic hydrosulphide*. *Potassic ferrocyanide* (or yellow prussiate) gives a pale blue precipitate, which, on exposure to the air, deepens in tint, owing to the absorption of oxygen. *Potassic ferricyanide* (or red prussiate), when added to a neutral or acid solution, gives a bright-blue precipitate, which is one of the varieties of Prussian blue ( $\text{Fe}_32\text{FeCy}_6, x\text{H}_2\text{O}$ ). If a solution of a ferrous salt be boiled with *nitric acid*, the metal is completely converted into a ferric salt: the same thing is effected by the action of chlorine or of bromine, or by boiling an acidulated solution of the salt with a small quantity of potassic chlorate.

2. *Ferric salts, or Persalts, or Salts of the peroxide*.—In solution they have a yellow or reddish-brown colour. *Hydrosulphuric acid* reduces them to the state of ferrous salts, whilst a white deposit of sulphur occurs: for example, with ferric sulphate the following reaction takes place:  $2(\text{Fe}'''_2\text{SO}_4) + 2\text{H}_2\text{S} = 4\text{Fe}''\text{SO}_4 + 2\text{H}_2\text{SO}_4 + \text{S}_2$ . With *ammonic hydrosulphide* a black hydrated ferric sesquisulphide is precipitated. The *hydrated alkalis* give a reddish-brown voluminous precipitate of hydrated sesquioxide, insoluble in excess of alkali. *Potassic sulphocyanide* in neutral or acid solutions gives an intense blood-red solution; *potassic ferrocyanide*, a bright blue precipitate of Prussian blue ( $\text{Fe}_32\text{FeCy}_6, x\text{H}_2\text{O}$ ). *Potassic ferricyanide* occasions no precipitate in solutions of the ferric salts, but the liquid acquires a greenish hue; the ferric salts may thus be distinguished from the ferrous salts. *Tincture of galls*, in neutral solutions, yields a bluish-black inky precipitate; it is the colouring matter of ordinary writing-ink; this test is rendered much more delicate in its indications by the addition of water holding a little calcic carbonate in solution in carbonic acid. In neutral solutions the *benzoates* and the *succinates* of the alkali-metals give voluminous insoluble precipitates: benzoate or succinate of ammonium or potassium has been employed to separate iron from nickel and cobalt, as the benzoates and the succinates of these metals are soluble. If a solution of a ferric

salt to which an alkali has been added till it begins to occasion a permanent precipitate be raised to the boiling-point, it is completely decomposed, and an insoluble basic ferric salt is precipitated: this property is often turned to account in the separation of iron from cobalt, nickel, and manganese, which are not precipitated under similar circumstances. When a ferric salt in solution is digested with a bar of zinc in a flask provided with a tube for the escape of the gas, the zinc becomes dissolved, hydrogen is evolved, and the whole of the iron is precipitated as sesquioxide, whilst a salt of zinc is formed in the liquid.

*Before the blowpipe* both classes of the salts of iron act alike: with borax in the reducing flame they give a green glass, which becomes colourless, or yellowish (if the iron be in large quantity) when held in the oxidating flame.

(774) *Estimation of Iron*.—In estimating the quantity of iron for the purposes of analysis, it should always be first converted into a ferric salt, by boiling with nitric acid or otherwise, after which it may be precipitated by excess of ammonia, and then well washed and ignited: pure ferric oxide remains, consisting in 100 parts of 70 of iron and 30 of oxygen. Iron is thus readily separated from the alkalis and alkaline earths. If magnesia be present, it is apt to be partially precipitated with the ferric oxide, unless the solution contain a considerable quantity of muriate of ammonia. In the presence of tartaric acid, of sugar, and of various other forms of organic matter, ammonia precipitates the ferric oxide very imperfectly from its solutions: in such a case ammoniac hydrosulphide must be employed. The iron is then thrown down completely as sulphide; this precipitate must be redissolved in nitric acid, and afterwards the iron may be obtained as sesquioxide by adding an excess of ammonia to the solution.

(775) *Separation of Iron from Aluminum and Glucinum*.—If alumina and glucina are contained in the liquid, they accompany the ferric oxide when precipitated by ammonia. When these earths are present, the precipitation should be effected by an excess of caustic potash instead of by ammonia; and the precipitate should be gently warmed with the liquid, for the purpose of dissolving out the earths. The solution is to be filtered from the ferric oxide, which requires long washing with boiling water to remove the last traces of potash. The alumina and glucina are obtained from the alkaline filtrate by neutralizing it with hydrochloric acid, and then adding a slight excess of ammonia; hydrated alumina and glucina are precipitated together, and must be separated in the manner already described (677).

(776) *Separation of Iron from Zinc, Cadmium, Cobalt, Nickel, and Manganese.*—Having precipitated the cadmium by sulphuretted hydrogen, and reconverted the iron into sesquioxide by boiling the liquid with a small quantity of nitric acid, the solution is to be largely diluted with water, and sodic carbonate added gradually to the acid liquid until a permanent precipitate is formed, though the liquid remains acid. The solution must be boiled, and the liquid filtered from the bulky precipitate of the basic ferric salt: the clear solution must then be slightly supersaturated with sodic carbonate, and afterwards feebly acidulated with acetic acid: on again boiling the liquid, the last trace of iron is thrown down in the form of basic acetate, whilst the other metals are retained in the solution: the precipitated ferric salt must be redissolved in hydrochloric acid, and the iron thrown down as sesquioxide by the addition of ammonia.

Sometimes ammonia in excess is made use of to separate iron from these metals, which all form soluble compounds with ammonia, and which it is supposed, will retain them in solution; but this method should never be resorted to in analysis, because the precipitated ferric oxide always carries down with it a large quantity of the other oxides.

(777) *Separation of Iron from Uranium.*—The iron having been converted into sesquioxide is precipitated by a large excess of ammoniac sesquicarbonate, which retains most of the uranium. This process, however, although usually adopted, is imperfect: for if the quantity of iron be at all large, a considerable proportion of uranium is precipitated along with it.

(778) *Estimation of Ferrous salt in a mixture of Ferric and Ferrous salts.*—It often happens that the chemist has to ascertain the relative proportions of ferrous and ferric oxide which a compound contains. If the compound of iron for examination be soluble in hydrochloric acid, the following process by Penny will be found both easy in execution and accurate in its results. It is based upon the power which a solution of the potassic dichromate (bichromate) in excess of hydrochloric acid possesses of converting ferrous chloride into ferric chloride, while the chromic acid is reduced to the state of chromic chloride;  $K_2Cr_2O_7 + 6FeCl_2 + 14HCl = 3Fe_2Cl_6 + Cr_2Cl_6 + 2KCl + 7H_2O$ . In order to carry this process into effect, 4.44 grms. of pure potassic anhydrodichromate are introduced into an alkalimeter burette of 100 cub. centim. (577), which is to be filled up to 0° with tepid water; the mixture is to be agitated until the salt is dissolved. Each division of the instrument contains sufficient of the dichromate

to convert 50 mgrms. of metallic iron, present in the form of ferrous chloride, into ferric chloride. The ore for experiment having been reduced to an extremely fine powder, 10 grammes of it are boiled in a flask for ten or fifteen minutes with about 80 cub. centim. of hydrochloric acid of sp. gr. 1.100: about 200 cub. centim. of boiling distilled water are added, and the mixture immediately transferred to an evaporating basin, taking care to rinse out the flask thoroughly. A white plate is then spotted over with a few drops of a weak solution of potassic ferricyanide, and the dichromate is cautiously added from the alkalimeter to the solution of iron (which is kept in continual agitation), until it assumes a dark-greenish shade; as soon as this begins to appear, it must be tested after each addition of the dichromate, by taking out a drop of the solution on a glass rod, and adding it to one of the drops of the ferricyanide. When the last drop no longer occasions a blue precipitate, the operation is ended, and the number of divisions of the liquid which has been added, when divided by two, indicates the amount of metallic iron which exists in the form of a ferrous compound in 100 parts of the ore. The total quantity of iron present in the solution may be ascertained by making a second experiment on a fresh portion of the ore, and reducing the metal whilst still in the flask with the hydrochloric acid, to the state of the ferrous salt: this is readily effected, either by transmitting a current of sulphuretted hydrogen and then expelling the excess of that gas by ebullition; or by boiling the concentrated solution with metallic zinc; or by nearly neutralizing the liquid with sodic carbonate, and adding a solution of sodic sulphite until a drop of the liquid ceases to give a red colour when mixed with a drop of a solution of potassic sulphocyanide,\* placed upon a white plate: the liquid is then boiled, to expel the excess of sulphurous acid. When the iron has thus been reduced to the state of ferrous salt, the whole quantity of the metal present may be ascertained by means of the solution of potassic dichromate, as before; the difference between the two results will give the per-centage of metallic iron present in the form of ferric salt.

Another excellent process for determining the amount of a ferrous salt present was contrived by Margueritte (*Ann. de Chimie*,

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\* The reducing effect of sodic sulphite on the ferric chloride may be explained by the following equation, from which it will be seen that the sodic sulphite is converted into sulphate during the operation;  $\text{Fe}'''_2\text{Cl}_6 + \text{H}_2\text{O} + \text{Na}_2\text{SO}_3 = 2\text{Fe}''\text{Cl}_3 + 2\text{HCl} + \text{Na}_2\text{SO}_4$ .

III. xviii. 244). It consists in ascertaining the quantity of a measured solution of potassic permanganate of known strength, which the cold acidulated and largely diluted solution of iron in hydrochloric acid, can deoxidize and deprive of colour, owing to the reaction expressed in the following equation;  $2\text{KMnO}_4 + 10\text{Fe}''\text{Cl}_2 + 16\text{HCl} = 2\text{MnCl}_2 + 2\text{KCl} + 5\text{Fe}''\text{Cl}_3 + 8\text{H}_2\text{O}$ . The strength of the solution of permanganate is ascertained by dissolving 0.5 gramme of clean iron wire in boiling hydrochloric acid, diluting the solution largely, and ascertaining the number of divisions of permanganate measured from a burette, which it is capable of decolorizing.

The total quantity of iron present in an ore or other compound may be ascertained by a second experiment upon a fresh portion of the ore, reducing the iron to the state of a ferrous salt by means of zinc, or otherwise, as described when treating of Penny's process.

(779) *Analysis of Cast Iron, Steel, and Bar Iron.*—For this purpose the metal must be reduced to a fine state of subdivision by means of a new file, previously freed from oil by the action of a solution of potash; the fine particles detached are to be sifted through a lawn sieve. Some kinds of cast iron are too hard to admit of being filed; they must be crushed in a small mortar made of hard steel.

1. The proportion of *carbon* is ascertained by mixing from 3 to 6 grammes of finely-divided iron with about 10 times its weight of plumbic chromate or of cupric oxide; then placing it in an apparatus similar to that shown in fig. 298, p. 82, and burning the iron in a very gentle current of oxygen: the carbonic anhydride which is formed is collected in a solution of potash placed in Liebig's bulbs. The tube which contains the iron is gradually heated with charcoal, commencing at the extremity nearest the potash bulbs, and the fire is slowly advanced towards the other end, until, when the operation is completed, the whole length of the tube is red hot. From the quantity of carbonic anhydride thus obtained, the proportion of carbon in the iron may be calculated.\* But it has been already explained that cast iron contains carbon partly in chemical combination, partly in a state of mechanical mixture, and it is important to determine the relative proportions of the carbon which exist in these different conditions. This may be effected by dissolving the iron in hydrochloric acid. In this operation all the carbon which was chemically combined with the iron is separated in the form either of a gaseous compound of carbon and hydrogen, or as a liquid hydrocarbon; whilst the scales of graphite mechanically diffused through the metal are not acted upon by the acid, and are left in a solid form mixed with silica. In order to ascertain the proportion of graphite in this residue, it is collected on a small weighed filter, and washed with ether, to remove any adhering

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\* A less rapid but accurate plan consists in digesting the iron in filings or in fragments with an excess of normal cupric chloride ( $\text{CuCl}_2$ ) dissolved in water; the iron is slowly dissolved, and copper precipitated in its place, whilst the carbon is left in a finely-divided condition. The precipitate must be collected on a filter, dried, and transferred to a tube in which it is, burned, as above directed.



liquid hydrocarbon; the filter and its contents are dried at  $100^{\circ}\text{C}$ ., and weighed in a covered crucible. The residue is then burned, and the silica which remains is deducted from the weight of the precipitate collected on the filter.

2. *Nitrogen*.—Two methods were employed by Boussingault for ascertaining the amount of nitrogen: the first consisted in oxidizing a known weight of iron (by heating it to redness) in a current of steam, condensing the water after it had passed over the iron, and determining the amount of ammonia that it contained, by a method previously contrived by him for ascertaining its amount in rain-water: the second consisted in converting a given weight of iron into sulphide, by heating it with cinnabar, and measuring the amount of nitrogen in the gaseous state by a method exactly analogous to that invented by Dumas for determining the amount of nitrogen in an organic body. For details, the reader is referred to the papers in the *Comptes Rendus* (lii. pp. 1008 and 1250).

3. The quantity of *silicon* contained in the iron is ascertained by dissolving the metal in hydrochloric acid and evaporating the solution to dryness, moistening with concentrated hydrochloric acid, then dissolving all the soluble matter in water, and collecting the silica in a filter: from this residue, after the graphite is burned off, the quantity of silicon can be estimated, 100 parts of silica representing 46.66 of silicon.

4. *Sulphur, Phosphorus, and Arsenicum*.—The most accurate mode of estimating these substances consists in deflagrating about 3 grammes of finely powdered iron with about six times its weight of a mixture of 5 parts of pure nitre, and 1 part of potassic carbonate, in a crucible of silver, or, still better, of gold.\* The phosphorus, sulphur, and arsenicum are thus converted into phosphoric, sulphuric, and arsenic anhydrides, which form salts by their action upon the potash; when the fused mass is digested in water they are dissolved, whilst the ferric oxide remains undissolved. The filtered solution is supersaturated with hydrochloric acid, and the sulphuric acid is thrown down by means of baric chloride; the excess of barium is removed by adding sulphuric acid, and the arsenic is thrown down as orpiment by a current of sulphuretted hydrogen. The liquid, filtered from the orpiment, is now neutralized by ammonia, and on the addition of a few drops of solution of magnesian sulphate, the phosphoric acid is gradually separated, on standing, as the crystalline ammonio-magnesian phosphate.

The ferric oxide is dissolved in hydrochloric acid, and a current of sulphuretted hydrogen is transmitted, by which copper would be separated as sulphide; the filtrate is boiled with nitric acid, and the iron separated from manganese, cobalt, or nickel, by means of sodic carbonate in the manner already described (776).

§ V. CHROMIUM: ( $\text{Cr} = 52.5$ ). *Sp. Gr.* 6.81; *Dyad, in Chromous Salts, as  $\text{CrCl}_2$ ; Triad, in Chromic Salts, as  $\text{Cr}_2\text{Cl}_3$ , occasionally Hexad, as in  $\text{CrF}_6$ .*

(780) CHROMIUM is a metal which is but sparingly distributed over the earth. Its most important ore is the chrome ironstone, a compound of ferrous oxide with chromic oxide ( $\text{FeO}, \text{Cr}_2\text{O}_3$ ), which is generally found massive, but has now and then been met with crystallized in regular octohedra like the magnetic oxide of iron, to which it corresponds in composition: it is principally

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\* Any traces of vanadium or of chromium would also be oxidized, and on digesting the mass in water would be dissolved out in the alkaline liquid.

supplied from North America and from Sweden. Occasionally the metal occurs in a higher state of oxidation, in combination with lead, as plumbic chromate ( $\text{PbCrO}_4$ ). Indeed it was in this beautiful mineral that Vauquelin, in the year 1797, first discovered the existence of chromium.

To obtain the metal, chromic oxide is intimately mixed, in fine powder, with charcoal, and made up into a paste with oil; it is then placed in a crucible lined with charcoal, and the cover of the crucible is luted on, after which it is exposed for two hours to the heat of a good wind furnace: an agglomerated mass of metallic appearance is thus obtained. It is not pure chromium, but consists of a combination of carbon with the metal. Chromium obtained by this method is very difficult of fusion: it generally forms a porous mass composed of brilliant grains, which are hard enough to scratch glass. In this state it has a specific gravity of about 5.9, which is no doubt lower than it would be after complete fusion. Deville found, on reducing chromium from pure sesquioxide by means of charcoal from sugar, in quantity sufficient for complete reduction, that the mass underwent partial fusion, but could not be melted into a complete button even at a temperature sufficient to fuse and volatilize platinum. If ignited with the hydrated alkalies, alkaline carbonates, or nitrates, chromium is rapidly converted into a chromate by action on the alkaline base. It may, however, be heated to redness in the open air without becoming oxidized, and is not acted on by any acid except hydrofluoric acid.

Freymy transmits the vapour of sodium over chromic chloride, which is placed in a porcelain tray, and heated to redness in a porcelain tube: the chromium is obtained in brilliant crystals, which belong to the regular system; they are insoluble in aqua regia. Wöhler reduces chromium from the violet chloride by fusing it with twice its weight of zinc under a flux of the mixed potassic and sodic chlorides: nitric acid is employed to dissolve the zinc, and the chromium is left as a grey brilliant crystalline powder of sp. gr. 6.81. If chromic chloride be mixed with potassium, and heated in a covered crucible, another modification of chromium may be procured; after washing the residue with water, the metal remains in the form of a dark-grey powder; which assumes a metallic lustre under the burnisher. This pulverulent chromium, if heated in the air, takes fire below redness, and burns brilliantly: it is oxidized with great violence by nitric acid, sometimes becoming incandescent during the action; and it is dissolved by hydrochloric acid and diluted sulphuric acid, with evolution of hydrogen.

Metallic chromium has not been applied in the arts, but its sesquioxide and many of the chromates are highly valued as colouring materials, both in painting on porcelain and in calico-printing.

(781) COMPOUNDS OF CHROMIUM WITH OXYGEN.—Chromium forms four well-marked oxides: a protoxide,  $\text{CrO}$ , and a sesquioxide,  $\text{Cr}_2\text{O}_3$ , both capable of forming salts with acids; an intermediate oxide ( $\text{CrO}, \text{Cr}_2\text{O}_3$ ), corresponding to the magnetic oxide of iron; and a stable anhydride ( $\text{CrO}_3$ ) which by its action on bases forms salts corresponding to the manganates and ferrates. It also appears to be probable that a perchromic acid ( $\text{HCrO}_4$ ) exists; at least, a blue liquid, which is soluble in ether, is ob-

tained on pouring hydric peroxide into a solution of chromic acid; but none of its compounds are known.

*Chromous oxide*, or *Protoxide of chromium* ( $\text{CrO} = 68.5$ ).—This oxide is known only in the hydrated condition. It is obtained as a dark-brown precipitate on adding caustic potash to a solution of the chromous chloride; it absorbs oxygen with great avidity, and even decomposes water with extrication of hydrogen, and then becomes converted into the intermediate hydrated oxide ( $\text{CrO}, \text{Cr}_2\text{O}_3, \text{H}_2\text{O}$ ), which is of the colour of Spanish snuff. (Péligot, *Ann. de Chimie*, III. xii. 541.)

Chromous oxide forms a double sulphate with potassic sulphate ( $\text{Cr}''\text{K}_2\text{SO}_4, 6\text{H}_2\text{O}$ ), corresponding to the ferroso-potassic sulphate both in form and composition. The crystals are of a fine blue colour.

(782) **CHROMIC OXIDE**, or *Sesquioxide of chromium*, ( $\text{Cr}_2\text{O}_3 = 153$ ); *Sp. Gr. cryst.* 5.21; *Comp. in 100 parts*, Cr, 68.68; O, 31.32.—This oxide is obtained as a greyish-green hydrate, by boiling with alcohol a solution of potassic dichromate (bichromate) acidulated with sulphuric acid. The alcohol deprives the chromic acid of half its oxygen, and the liquid becomes green from the formation of chromic sulphate. A current of sulphurous anhydride may be employed instead of alcohol in the reduction of chromic acid. On the addition of ammonia, a bulky, gelatinous, bluish-green precipitate of the hydrated sesquioxide is produced, which retains alkali with great obstinacy even when boiled with water. In this form it is freely soluble in acids, and forms salts, the solutions of which are of a green colour; but they do not crystallize.

Chromic oxide gives rise also to another set of soluble salts, which are of a violet colour and crystallize readily. When these violet-coloured salts are precipitated by ammonia, they give a bluish-green hydrated sesquioxide, which if redissolved in an acid without the application of heat, reproduces the violet-coloured salts. This precipitated oxide becomes green by the action of concentrated saline solutions upon it. If a solution of one of the violet salts be heated to the boiling-point, or a little short of it, the salt at once becomes green.

This change of colour from violet to green has been long known, and was accounted for by Berzelius upon the admission of two distinct hydrates of chromic oxide, one green, the other violet. But Siewert appears to have distinctly proved that one form only of the sesquioxide, the blue hydrate, exists. The green precipitate in every instance is a compound of the pure oxide with potash or soda. It is true that the violet solutions of the pure salts become green by boiling, but this Siewert has traced to the conversion of the normal salt into two soluble salts, each green, and capable of co-existing in the liquid. One of these salts contains excess of acid, the other excess of base (*Liebig's Ann.* cxxvi. 86). Solutions of the green salts at once become blue or violet, if acidulated by the addition of nitric acid. The investigation of these compounds is beset with unusual difficulties.

The hydrated sesquioxide from the violet salts is the *metachromic* oxide of Fremy ( $\text{Cr}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ , when dried *in vacuo*), and is soluble in excess of ammonia in presence of acetic acid: but according to Siewert, who has lately examined this precipitate with great care, it is not a pure sesquioxide, but a compound of the hydrated sesquioxide with ammonia and one of the salts of ammonium. It is soluble in excess of ammonia and acetic acid, owing to the strong tendency of chromic oxide and ammonia to produce, in the presence of acetic acid, double salts, which are not susceptible of decomposition by ammonia. If the original precipitate be thoroughly washed till all the soluble salts are removed from it, and then air dried, it is no longer soluble in acetic acid, or in other diluted acids.

The only way to ensure the production of a pure hydrated chromic oxide, according to Siewert, consists in precipitating a soluble chromic salt by the addition of ammonia, and boiling it with excess of the alkali. A light-blue precipitate is thus obtained, which, when well washed and dried in air over oil of vitriol, consists of ( $\text{Cr}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ ). If dried *in vacuo*, it retains only  $4\text{H}_2\text{O}$ , and if dried in a current of hydrogen at  $392^\circ$  ( $200^\circ \text{C.}$ ) it retains  $\text{H}_2\text{O}$ ; it then forms a blue powder with a greenish lustre, and is insoluble in boiling diluted hydrochloric acid. Caustic potash and soda precipitate the hydrated sesquioxide, and redissolve it if added in excess, forming a green solution, from which, on boiling, the whole of the chromic oxide is separated as a green hydrate, which retains a portion of alkali. Indeed, potash and soda have so strong a tendency to combine with chromic oxide that if either of these alkalies be used to precipitate the oxide from its salts, or if salts of potash or soda be present when ammonia is employed as the precipitant, the green precipitate always contains one of the fixed alkalies. When the hydrated sesquioxide is heated, it parts with its water below redness, and if heated a little beyond this point, it suddenly becomes incandescent, and shrinks considerably in bulk, after which it is no longer attacked by acids.

Besides the soluble variety of the salts of chromium, an anhydrous, insoluble series is known, corresponding, it would seem, to the dense and comparatively inert modification of the metal itself.

Anhydrous green chromic oxide is not decomposed by heat, and hence is used as a green colour in enamel painting. It is usually prepared for this purpose by decomposing basic mercurous chromate by a red heat: half the oxygen of the anhydride is expelled along with the mercurous oxide. Ammonic chromate may be employed instead of mercurous subchromate with equally good results. Another method consists in igniting strongly, in a covered crucible, an intimate mixture of 4 parts of powdered potassic chromate and 1 part of starch; the potassic carbonate

resulting from the decomposition is washed out, and the chromic oxide which remains, after undergoing a second calcination, yields a beautiful clear green colour. There are also a variety of other modes of obtaining it. Chromic oxide is the colouring ingredient in greenstone, in the emerald, in pyrope, and in several other minerals. The *pink colour* used on earthenware is prepared by heating to redness a mixture of 30 parts of stannic oxide, 10 of chalk, and 1 part of potassic chromate; the product is then finely powdered, and washed with weak hydrochloric acid; a beautiful rose-tint is thus obtained.

A beautiful green pigment known as *vert de Guignet* is manufactured on a large scale by calcining potassic dichromate with 3 times its weight of crystallized boracic acid: oxygen and water are expelled, and on washing the residue with water a basic chromic borate is left, while boracic acid and potassic borate are dissolved out.

(783) *Chrome iron-stone* ( $\text{FeO}, \text{Cr}_2\text{O}_3$ ; *Sp. Gr.* 4.5) is the principal ore of chromium: it corresponds in composition to brown oxide of chromium and to the magnetic oxide of iron; part of the iron is, however, generally displaced by the isomorphous metal magnesium, and part of the chromium by aluminum. Like magnetic iron ore, chrome iron-stone often crystallizes in octohedra, which have about the same hardness as felspar. Chrome iron-stone is scarcely attacked by any of the acids. It is infusible in the furnace, and when heated absorbs oxygen from the air; this oxidation takes place rapidly when it is powdered and mixed with a carbonate of one of the metals of the alkalis or alkaline earths, a chromate of the base being formed. 100 parts of this ore, if pure, contain 48.27 of chromium, and correspond to 89.6 of chromic anhydride.

(784) Fremy believes in the existence of a series of ammoniated compounds of chromium presenting some analogy with those of cobalt, but other chemists have not confirmed his results. If a solution of sal ammoniac containing free ammonia be digested on the hydrated sesquioxide precipitated by ammonia from one of the violet chromium salts, the oxide is dissolved, and a fine violet-coloured solution is formed, owing to the formation of an ammonio-chromic double salt. If the solution be evaporated to dryness, it furnishes a fine violet compound, which is very soluble in water, has scarcely any alkaline reaction, and gives no precipitate with argentic nitrate; the ordinary tests of chromium do not show the presence of the metal. When the solution is boiled, ammonia is expelled and hydrated chromic oxide is precipitated.

(785) CHROMIC ANHYDRIDE, formerly *Chromic acid* ( $\text{CrO}_3 = 100.5$ ); *Sp. Gr.* 2.676.—There are several modes of obtaining this compound. 1.—The simplest consists in mixing 4 measures of a cold saturated solution of potassic dichromate with 5 of oil of vitriol: as the liquid cools, the chromic anhydride separates in beautiful crimson needles; for though very soluble in water, this

compound has the peculiarity of being nearly insoluble in sulphuric acid of sp. gr. 1.55, but is freely dissolved by it either in a more concentrated or in a more dilute condition. The crystals are allowed to dry upon a porous tile, under a bell-glass. A good deal of sulphuric acid, however, still adheres to them; in order to remove it, the crystals should be dissolved in water, and a solution of baric dihydro-chromate ( $\text{BaH}_2\text{CrO}_4$ ) should be added in quantity just sufficient to throw down the whole of the sulphuric acid as baric sulphate: the solution may be recrystallized by evaporation *in vacuo*. 2.—Chromic anhydride may also be prepared from the chromic hexafluoride ( $\text{CrF}_6$ ), by decomposing this compound with water (790).

Chromic anhydride is easily freed from water by drying it at a gentle heat. While hot it is black, but it becomes dark red on cooling: at about  $392^\circ$  ( $200^\circ \text{C.}$ ) it fuses, and if heated more strongly becomes vividly incandescent, and is converted into the sesquioxide with disengagement of oxygen. The anhydride deliquesces when exposed to the air. Its solution has a sour, metallic taste, and possesses considerable oxidizing power, from the facility with which it is reduced to chromic oxide. When heated with hydrochloric acid, chlorine is evolved and chromic chloride is formed;  $2\text{CrO}_3 + 12\text{HCl} = \text{Cr}_2\text{Cl}_6 + 6\text{H}_2\text{O} + 3\text{Cl}_2$ . The anhydride forms more than one crystalline compound with sulphuric acid; these compounds are decomposed by water.

(786) *Chromates*.—Chromic acid is dibasic; it forms 3 classes of salts—basic, normal, and acid. The chromates of the alkali-metals are soluble in water; the normal salts have the general formula  $\text{M}'_2\text{CrO}_4$ ; they have a yellow colour; the acid salts are of a bright orange: the most important of these salts are the potassic chromate, and the anhydrous chromate or dichromate, from which the other chromates are generally obtained. Chromic acid is, like iodic acid, remarkable for the anhydro-salts which it forms with potash; it yields four salts with this base, known respectively as: 1, the chromate ( $\text{K}_2\text{O}, \text{CrO}_3$ ); 2, the dichromate or bichromate ( $\text{K}_2\text{O}, 2\text{CrO}_3$ ); 3, the trichromate ( $\text{K}_2\text{O}, 3\text{CrO}_3$ ); and 4, the tetrachromate of potash ( $\text{K}_2\text{O}, 4\text{CrO}_3$ ).

*Potassic dichromate*, or *Anhydro-chromate*, or *Bichromate of potash* ( $\text{K}_2\text{O}, 2\text{CrO}_3$ , or  $\text{K}_2\text{Cr}_2\text{O}_7 = 295.2$ ); *Sp. Gr.* 2.624; *Comp. in 100 parts*,  $\text{K}_2\text{O}$ , 31.93;  $\text{CrO}_3$ , 68.07.—This salt crystallizes in large red, transparent, anhydrous four-sided tables. It fuses below redness, and as it cools splits to pieces from the inequality of its contraction. By heating the anhydro-chromate to bright redness, normal potassic chromate and green chromic oxide are

formed, whilst oxygen escapes. It requires about 10 times its weight of water at  $15^{\circ}$  C. for its solution.

In order to procure potassic anhydro-chromate, chrome iron-stone is heated to redness and quenched in cold water, by which means it is rendered friable, and is then reduced to an extremely fine powder, and heated to bright redness in a current of air in a reverberatory furnace with a mixture of chalk and potassic carbonate, the mixture being constantly stirred to hasten the oxidation. When this is complete, the product is digested in water, potassic carbonate being added, if necessary, to decompose any calcic chromate which may have been formed, and the yellow solution is drawn off from the insoluble matter; it is then supersaturated with nitric acid; a portion of silica is thus precipitated, and after this has been separated, the liquid, on evaporation, yields crystals of potassic anhydro-chromate, which are purified by recrystallization. The addition of chalk in the furnace favours the oxidation by preserving the mass in a porous condition: if potash alone were used, it would fuse, and the chrome ore would fall to the bottom.

According to Schweitzer, several double salts may be formed by digesting potassic dichromate with an equivalent of some base, such as lime or magnesia. The magnesio-potassic chromate crystallizes in oblique rhombic prisms ( $K_2Mg_2CrO_4 \cdot 2H_2O$ ), and a similar calcicopotassic chromate may be obtained; but there is no analogy between these double chromates and the magnesian double sulphates.

If a solution of potassic carbonate be added to the anhydro-chromate, until it becomes of a pale yellow colour, carbonic anhydride is expelled, and the *normal potassic chromate* ( $K_2CrO_4 = 194.7$ ; *sp. gr.* 2.682) is formed. This salt is soluble in about twice its weight of cold water, and still more freely so in boiling water; it has a pure and intense yellow colour. A very small quantity of the salt suffices to impart a yellow tinge to a considerable volume of water. By evaporation of its solution potassic chromate may be obtained with some difficulty in transparent, yellow, anhydrous prisms, which are isomorphous with those of potassic sulphate: at a red heat it fuses without undergoing decomposition. A *trichromate* ( $K_2O_3CrO_3$ ), also anhydrous, was obtained by Mitscherlich in deep red crystals, by adding an excess of nitric acid to a solution of the dichromate, and allowing it to evaporate. Siewert has obtained a *tetrachromate* ( $K_2O_4CrO_3$ ) in thin, red, brilliant prismatic plates, by evaporating a solution of the trichromate in nitric acid at a gentle heat.

*Sodic chromate* ( $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O} = 162.5 + 180$ ) may be obtained by a process similar to that employed in preparing potassic chromate: it forms efflorescent crystals: a *hydro-sodic chromate* ( $\text{NaHCrO}_4 \cdot \text{H}_2\text{O}$ ) may likewise be obtained in ruby red crystals.

*Calcic chromate* is soluble, as is also the *acid-chromate*, which is formed in many chrome works as a preliminary stage in the manufacture of the chromates. Jacquelin decomposes chrome ore by roasting it in fine powder intimately mixed with chalk, grinds the roasted mass with water, and adds sulphuric acid till the liquid has an acid reaction, in which case dihydro-calcic chromate is formed, and remains in solution. *Baric chromate* ( $\text{BaCrO}_4 = 253.5$ ; *sp. gr.* 3.90) is a canary-yellow insoluble powder. *Strontic chromate* is yellow and but slightly soluble.

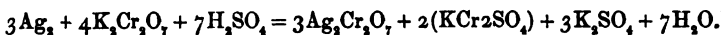
*Plumbic chromate*, or *Chromate of lead* ( $\text{PbCrO}_4 = 323.5$ ; *sp. gr.* 5.653) forms the pigment called 'chrome yellow.' It is obtained by precipitating a somewhat dilute solution of plumbic acetate by one of potassic chromate or dichromate. Plumbic chromate is insoluble in water and in acids, but like all the insoluble lead salts, it is dissolved by a large excess of potassic or sodic hydrate. When heated to  $392^\circ$  ( $200^\circ$ ) or  $482^\circ$  ( $260^\circ \text{C.}$ ), its colour becomes reddish brown; at a higher temperature it fuses, and when heated still more strongly it gives off about 4 per cent. of oxygen, chromic oxide, and basic plumbic chromate being formed;  $8\text{PbCrO}_4 = 4(\text{PbCrO}_4 \cdot \text{PbO}) + 2\text{Cr}_2\text{O}_3 + 3\text{O}_2$ . Fused plumbic chromate when reduced to powder is sometimes advantageously substituted for cupric oxide in the combustion and analysis of organic substances very rich in carbon. A *dibasic plumbic chromate* ( $2\text{PbO} \cdot \text{CrO}_3$ ; *sp. gr.* 6.266), of a splendid scarlet colour, may be obtained by boiling a solution of the yellow plumbic chromate with half an equivalent of lime, or by adding to a solution of plumbic nitrate a solution of potassic chromate, with which an additional equivalent of potassic hydrate has been previously mixed. It may be obtained of a still more brilliant colour by fusing one part of the normal plumbic chromate with 5 parts of nitre; potassic chromate and dibasic chromate of lead are formed; the potassium salt may be removed by washing. The salt is used to impart a permanent orange to calico: it is easily formed upon the fabric by first dyeing it yellow with normal chromate of lead, and then boiling it with lime-water, by which half the chromic acid is abstracted, and the dibasic chromate is left attached to the fibre.

*Basic mercurous chromate* ( $3\text{Hg}_2\text{CrO}_4 \cdot \text{Hg}_2\text{O}$ ) falls as an orange-coloured insoluble precipitate on adding basic mercurous nitrate to a soluble chromate. *Argentichromate* ( $\text{Ag}_2\text{CrO}_4$ ; *sp. gr.* 5.77) is of a dark-red colour, the tint of which is deeper if the solutions be mixed whilst hot: it is crystalline, and sparingly soluble.

An *argentic anhydro-chromate* ( $\text{Ag}_2\text{O} \cdot 2\text{CrO}_3$ ) is obtained in beautiful crimson



tables by heating metallic silver with potassic anhydro-chromate and sulphuric acid, chrome-alum being formed during the process :—



Chromic acid is the colouring matter of the ruby.

*Bichromate of chloride of potassium* ( $\text{KCl}, \text{CrO}_3$  ? or  $\text{K}_2\text{CrO}_4, \text{CrO}_3, \text{Cl}_2$ ; *Sp. Gr.* 2.466).—This remarkable compound may be obtained crystallized in orange-coloured needles, by dissolving 3 parts of potassic anhydro-chromate and 4 of hydrochloric acid in a little water at a gentle heat, and allowing it to cool: a large quantity of water decomposes the salt.

(787) *Chromic sesquisulphide* ( $\text{Cr}_2\text{S}_3 = 201$ ).—This compound may be obtained in black shining scales, resembling plumbago in appearance, when the vapour of carbonic disulphide is transmitted over chromic oxide strongly heated in a porcelain tube. The attraction of chromium for sulphur is but slight. If ammoniac hydrosulphide be mixed with a chromic salt, the hydrated sesquioxide of the metal is precipitated, whilst sulphuretted hydrogen is evolved.

(788) **COMPOUNDS OF CHROMIUM WITH CHLORINE.**—Chromium forms two chlorides, chromous chloride,  $\text{CrCl}_2$ , and chromic chloride,  $\text{Cr}_2\text{Cl}_6$ : the latter is the more important. It also forms an oxychloride ( $\text{CrCl}_2\text{O}_2$ ), frequently termed chlorochromic acid.

*Chromous chloride* (Péligot's protochloride,  $\text{CrCl}_2 = 123.5$ ) is obtained by heating the chromic chloride to redness in a current of dry hydrogen (carefully freed from every trace of oxygen); it is a white substance which is readily dissolved by water, forming a blue solution which absorbs oxygen rapidly, and becomes green: like ferrous chloride, it absorbs nitric oxide quickly and becomes brown.

*Chromic chloride*, formerly *Sesquichloride of chromium* ( $\text{Cr}_2\text{Cl}_6 = 318$ ).—When a current of dry chlorine is transmitted over an intimate mixture of finely-divided chromic oxide and charcoal, heated to redness in a glass tube, beautiful pale violet-coloured scales of anhydrous chromic chloride sublime. When rubbed upon the skin they have a soapy feel; they are quite insoluble in cold water, but by boiling them with water for some time, a green solution is gradually formed. Sulphuric and hydrochloric acids, and even aqua regia, do not dissolve them. It is, however, very remarkable that the change from this insoluble to the soluble green variety is effected in a few moments with extrication of heat, by the addition of a minute quantity of the chromous chloride to the insoluble chloride when it is suspended in water. When the green hydrated chromic oxide is dissolved in hydrochloric acid a similar green solution is formed: the liquid furnishes, by spontaneous evaporation, green crystals, which may be represented, according to Péligot, as consisting of  $(\text{Cr}_2\text{O}_3, \text{Cl}_2, 4\text{HCl}, 10\text{H}_2\text{O})$ ; for it is singular that only two-thirds of the chlorine which this solution contains is precipitated when it is mixed with argentic nitrate (*Ann. de Chimie*, III. xii. 536,

xiv. 239, and xvi. 294). A soluble violet chloride of the metal which contains the same proportion of chlorine may be formed by precipitating the violet-coloured chromic sulphate by an equivalent quantity of baric chloride: argentic nitrate precipitates the whole of the chlorine from this solution.

Several oxychlorides of chromium may be formed.

(789) *Chromic oxydichloride*, or *Chlorochromic acid* ( $\text{CrCl}_2\text{O}_2$ ); *Sp. Gr. of vapour*, 5.52; *of liquid*, 1.71; *Mol. vol.*  $\square$ ; *Boiling-pt.*  $255^\circ$  ( $121^\circ.1$  C.).—This is a dense red liquid, which emits copious red fumes, of a suffocating odour; it is immediately decomposed by water into chromic and hydrochloric acids. When dropped into a strong solution of ammonia or into alcohol, it bursts into flame from the intensity of the reaction. If the vapour be passed through a tube of porcelain heated to redness, beautiful rhombohedral crystals of chromic oxide are formed: these crystals are isomorphous with those of corundum; they are hard enough to cut glass, and are of a very dark green colour. During their formation, oxygen and chlorine escape, in consequence of the following reaction;  $4\text{CrCl}_2\text{O}_2 = 2\text{Cr}_2\text{O}_3 + 4\text{Cl}_2 + \text{O}_2$ .

Chlorochromic acid is analogous to the chloromolybdic, chlorotungstic, and chlorosulphuric acids in composition, and in the products which it yields when decomposed. In order to prepare it, 10 parts of common salt are fused with 17 of potassic chromate; the melted mass, when cold, is broken into fragments, and gently heated in a retort with 30 parts of oil of vitriol: the chlorochromic acid distils over readily.

(790) **CHROMIC HEXAFLUORIDE**, or *Fluoride of chromium* ( $\text{CrF}_6$ , = 166.5), is obtained by distilling 4 parts of plumbic chromate, 3 of powdered fluor-spar, and 8 of strong sulphuric acid, in a platinum retort; sulphates of lead and calcium are formed, and the hexafluoride distils as a deep red vapour, which by a low temperature is reduced to a blood-red liquid;  $\text{PbCrO}_4 + 3\text{CaF}_2 + 4\text{H}_2\text{SO}_4 = \text{PbSO}_4 + 3\text{CaSO}_4 + 4\text{H}_2\text{O} + \text{CrF}_6$ . Any other chromate may be substituted for plumbic chromate in this operation.

Chromic hexafluoride forms deep-red fumes of chromic anhydride the moment that it comes into the air, as it is instantly decomposed by moisture: by conducting the vapour into a moistened platinum crucible the vessel becomes speedily filled with voluminous crystals of chromic anhydride; hydrofluoric acid is formed at the same time, and may be expelled from the chromic anhydride by a gentle heat. The action of water upon the hexafluoride may be thus represented;  $\text{CrF}_6 + 3\text{H}_2\text{O} = \text{CrO}_3 + 6\text{HF}$ .

(791) **NITRIDE OF CHROMIUM** ( $\text{Cr}_3\text{N}_4$ ?; Schrötter).—If the anhydrous violet chromic chloride be heated in a current of dry ammoniacal gas, ammoniac chloride sublimes, whilst the chromic chloride is decomposed, emitting a purple light, and an insoluble chocolate-brown compound of chromium and nitrogen is left. If it be heated to between  $302^\circ$  and  $392^\circ$  ( $150^\circ$  and  $200^\circ$  C.) in a current of oxygen, it takes fire and burns with a beautiful red light into chromic oxide, emitting nitrogen gas mixed with red fumes of peroxide of nitrogen.

(792) **CHROMIC SULPHATE** ( $\text{Cr}_2\text{SO}_4$ , = 393).—There are three varieties of this salt. One of them is a *green* soluble compound, which is freely dissolved by alcohol, but does not crystallize. It is viewed by Siewert as a mixture of a basic and an acid sulphate (*Liebig's Annal.* cxxvi. 95). It may be obtained by boiling hydrated chromic oxide with sulphuric acid. A second modifi-

cation, of a *violet* colour, may be procured by digesting 8 parts of the hydrated sesquioxide dried at  $100^{\circ}$  C. with 9 parts of oil of vitriol, in a shallow vessel exposed to the air at ordinary temperatures. The mixture absorbs water gradually, and becomes converted in two or three weeks' time into a greenish-blue mass of crystals: if these crystals are dissolved in water they form a blue liquid from which alcohol separates the salt in small octohedra containing  $15\text{H}_2\text{O}$ . This modification forms with potassic or ammoniac sulphate a beautiful violet double salt (chrome alum) which crystallizes by spontaneous evaporation in bold octohedra, and corresponds in form and composition to ordinary alum, the formula of the potassium-salt being  $(\text{KCr}_2\text{SO}_4, 12\text{H}_2\text{O})$ , sp. gr. 1.826. The solution of the violet sulphate, when boiled, becomes green; and if the crystals of chrome alum be dissolved in water, and the solution be boiled, the plum-coloured liquid also becomes green, and loses the power of crystallizing on cooling. If the violet sulphate be heated to  $100^{\circ}$  C. it melts in its water of crystallization, loses  $10\text{H}_2\text{O}$ , and becomes converted into the green salt: but if the temperature be raised to about  $698^{\circ}$  ( $370^{\circ}$  C.), both the green and the violet modification are rendered anhydrous, and a third salt is obtained in *red* crystals, which are no longer soluble in water, or even in concentrated acids, or aqua regia. If digested for a long time with water, however, it becomes converted into the soluble form (Schrötter, *Pogg. Annal.* liii. 513). The composition of these three sulphates would be represented as follows:—

Red insoluble sulphate . . .	$\text{Cr}_2\text{SO}_4$
Green soluble sulphate . . .	$\text{Cr}_2\text{SO}_4, 5\text{H}_2\text{O}$
Violet soluble sulphate . . .	$\text{Cr}_2\text{SO}_4, 15\text{H}_2\text{O}$

Several chromic subsulphates may also be formed.

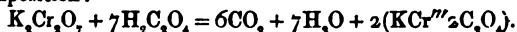
(793) CHROMIC NITRATE, or *Nitrate of chromium* ( $\text{Cr}_3\text{NO}_3$ ), is a green very soluble salt; when gently ignited, it loses its acid, and yields a brown oxide of chromium ( $\text{Cr}_2\text{O}_3$ ), which has been regarded as a chromate of sesquioxide of chromium;  $(\text{Cr}_2\text{O}_3, \text{Cr}_2\text{O}_3) = 3\text{Cr}_2\text{O}_3$ .

(794) CHROMIC OXALATES.—Ammoniac oxalate gives a green insoluble precipitate when mixed with a solution of green chromic chloride, but if the hydrated chromic oxide be digested with oxalic acid, a green soluble oxalate is formed.

Chromic oxalate forms two remarkable series of double salts, viz., *dark blue* salts, which form bluish-green solutions in water, with the general formula  $(\text{M}'_3\text{Cr}'''_3\text{C}_2\text{O}_4)$ , and *garnet-coloured* salts, which form cherry-red solutions in water, of the formula  $(\text{M}'\text{Cr}'''_2\text{C}_2\text{O}_4)$ . The *blue potassium-salt* ( $\text{K}_3\text{Cr}'''_3\text{C}_2\text{O}_4, 3\text{H}_2\text{O}$ ) may be obtained by boiling a solution of 19 parts of potassic anhydro-chromate, 23 of potassic oxalate, and 55 of crystallized oxalic acid: the chromic acid is reduced to the state of sesquioxide, and carbonic anhydride is evolved in abundance;  $\text{K}_3\text{Cr}_2\text{O}_7 + 2\text{K}_2\text{C}_2\text{O}_4 + 7\text{H}_2\text{C}_2\text{O}_4 = 6\text{CO}_2 + 7\text{H}_2\text{O} + 2(\text{K}_3\text{Cr}'''_3\text{C}_2\text{O}_4)$ . The

solution is evaporated to dryness, redissolved in water, and set aside to crystallize. The salt is deposited in large rhombic prisms which appear to be black by reflected light, and blue by transmitted light. They appear greenish when powdered, the solution is red by transmitted and green by reflected light: ammonia does not precipitate chromic oxide from the solution; potassic hydrate occasions no precipitate till the liquid is boiled. Corresponding salts may be obtained containing sodium, ammonium, barium, strontium, calcium, and magnesium instead of potassium, but these different salts vary in the proportion of water which they retain.

The *red potassium salt* ( $\text{KCr}'''2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ , or  $6\text{H}_2\text{O}$ ) may be procured by adding 55 parts of oxalic acid to a boiling concentrated solution of 19 parts of potassic anhydro-chromate, carbonic anhydride being expelled, owing to the following decomposition:—



It may be obtained by spontaneous evaporation crystallized in small rhomboidal tables, which are dark-red both by reflected and by transmitted light: the salt requires about 10 parts of cold water for solution, but is soluble to any extent in boiling water. The concentrated solution is dark-green or nearly black by reflected light, but red by transmitted light. Potassic hydrate gives no precipitate in the solution till raised to ebullition; neither does ammonia cause any separation of chromic oxide. An analogous salt may be formed with ammonium, ( $\text{H}_4\text{NCr}'''2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ ).

#### (795) CHARACTERS OF THE COMPOUNDS OF CHROMIUM:—

1.—The *chromous salts*, or *salts of the protoxide*, are but little known. They absorb oxygen rapidly from the air; they are sparingly soluble in water, and form either red or blue solutions, which, like those of the ferrous salts, absorb nitric oxide in large quantity, and form dark-brown solutions. With the chromous salts *potassic hydrate* gives a brown precipitate of hydrated chromous oxide; *ammonia*, a greenish-white precipitate, which, if ammoniac chloride be present, is redissolved by excess of ammonia, forming a blue liquid, which becomes red as it absorbs oxygen. With *potassic hydrosulphide* they give a black sulphide; and with *potassic ferrocyanide* a greenish-yellow precipitate. These salts reduce solutions of gold to the metallic state, and convert corrosive sublimate into calomel.

2.—The *chromic salts*, or *salts of the sesquioxide*, have a sweetish astringent taste, and are poisonous; their solutions redden litmus. They are either green or violet coloured; the green solutions generally transmit a red light. With *ammonia* they yield a bulky gelatinous precipitate of hydrated chromic oxide. *Caustic potash* and *soda* give a green precipitate, which is dissolved with a green colour in excess of the cold alkaline solution, but is re-precipitated completely by boiling the liquid, carrying down alkali with it. The *carbonates of the alkali metals* give a green precipitate which is redissolved by an excess of the alkaline liquid. *Sulphuretted hydrogen* gives no precipitate. The

*sulphides of the alkali-metals* precipitate the green chromic oxide, with escape of sulphuretted hydrogen. If any of these precipitates be fused with a mixture of nitre and potassic carbonate, it yields a yellow soluble potassic chromate.

3.—*The Chromates.*—*Before the blowpipe* in the reducing flame they colour borax and microcosmic salt green. When boiled with diluted sulphuric acid, to which a little alcohol or sugar has been added, they are decomposed, and the chromic acid is reduced to the green chromic sesquisulphate, and chromic oxide is precipitated with its characteristic colour on adding an excess of ammonia. An alcoholic tincture of guaiacum, 1 of resin to 100 of spirit, is turned blue by a very minute trace of free chromic acid (1 millionth part, Schiff), but the colour speedily disappears; an excess of sulphuric acid favours the reaction, which, though exceedingly delicate, is not characteristic, as it is produced by other oxidizing agents. Most of the chromates are strongly coloured. Many of them are insoluble in water, but they are nearly all readily dissolved by diluted nitric acid. Their solutions give a yellow precipitate with *lead salts*, a red with *argentic nitrate*, and an orange with *basic mercurous nitrate*: these precipitates are soluble in nitric acid, but not in acetic acid. When heated with oil of vitriol the chromates evolve oxygen; with hydrochloric acid they evolve chlorine. In both cases green chromic salts are formed. Workmen engaged in the manufacture of potassic anhydro-chromate are liable to the gradual destruction of the nasal bones, and to the occurrence of ulceration of the throat, in appearance a good deal resembling that occasioned by secondary syphilis. Small doses of corrosive sublimate have been found to act as an effectual remedy in such cases (Crace Calvert).

(796) *Estimation of Chromium, and Separation from the Alkalies and Alkaline Earths.*—Chromium may be most accurately estimated in the form of sesquioxide. It may be easily reduced to this condition, even if it exist in solution in the form of a chromate, by acidulating with hydrochloric acid, and transmitting a current of sulphuretted hydrogen: the liquid must then be boiled, and on the addition of ammonia to the hot solution the sesquioxide is precipitated. It is to be well washed, and ignited in a covered platinum crucible; 100 parts of the anhydrous oxide contain 68.63 of chromium. The presence of acetic acid prevents the precipitation of chromic oxide from its solutions by the addition of ammonia, even after long boiling.

The separation of chromium from the metals of the earths, and from zinc, cadmium, cobalt, nickel, and iron may be effected by fusing the mineral, or the precipitate obtained by ammonia from its solution in an acid, with a mixture of potassic carbonate and nitre; the chromium is thus converted into a soluble chromate, from which the chromium may be precipitated as directed in the foregoing paragraph, whilst the earths and the other metals remain in the insoluble portion, either in the form of oxides or of carbonates.

§ VI. MANGANESE: ( $Mn=55$ ). *Sp. Gr.* 8.013; *Dyad as in Manganous Salts,  $MnCl_2$ ; more rarely Triad as in Manganic Salts,  $Mn_2O_3$ .*

(797) THE ORES of this metal are tolerably abundant, and it enters, in greater or less quantity, into the composition of a vast number of minerals, so that it is widely diffused throughout the mineral kingdom. The most important and valuable ore of manganese is the black oxide, which occurs either massive or in radiated crystals.

Manganese was first recognized as a distinct metal by Gahn in 1774. It is reduced to the metallic state with difficulty. The best method consists in mixing manganous carbonate into a paste with oil and sugar, and introducing it into a crucible lined with charcoal, furnished with a cover luted on: it must at first be heated gently, to expel the volatile matters, and then ignited intensely for a couple of hours in the heat of a forge. It may thus be obtained in the form of a metallic globule which contains a variable quantity of carbon; the carbon may be removed by fusing the metal a second time in a porcelain crucible with a little manganous carbonate. A solution of manganous chloride also yields plates of the reduced metal when subjected to electrolysis.

Manganese is of a greyish-white colour, and is brittle, but hard enough to scratch steel; it is very feebly magnetic. By exposure to the air, it speedily becomes oxidated; it decomposes water slowly at ordinary temperatures, and should be preserved either in sealed tubes or under naphtha.

Manganese enters into combination with both carbon and silicon when fused with them: the carbide, when treated with acids, leaves part of the carbon as a black powder: the compound of manganese with silicon is decomposed with difficulty even by aqua regia, in which case it leaves a residue of silica.

Metallic manganese is not employed as such in the arts. It yields various alloys, but none of them are of practical importance, with the exception of its combination with iron, which is harder and more elastic than iron alone. The chief uses of the compounds of manganese are chemical, the black oxide being extensively employed to decompose hydrochloric acid and furnish chlorine. It likewise supplies the chemist with his cheapest source of oxygen, and is employed as a colouring material in the manufacture of glass and enamels. It is also used as a flux in the preparation of cast steel; and it furnishes a useful mordant to the calico-printer, when precipitated in the form of brown hydrate upon the fibre.

(798) OXIDES OF MANGANESE.—Manganese forms several compounds with oxygen. The protoxide,  $\text{MnO}$ , is a powerful base; the sesquioxide,  $\text{Mn}_2\text{O}_3$ , is feebly basic; the red oxide, a compound of these two,  $\text{MnO}, \text{Mn}_2\text{O}_3$ , is quite indifferent to the action of acids: so also is the deutoxide or black oxide,  $\text{MnO}_2$ : but the two higher oxides have well-marked acid characters. The general formula for the salts of manganic acid is  $\text{M}'_2\text{MnO}_4$ , and for those of permanganic acid  $\text{M}'\text{MnO}_4$ . Neither of these acid oxides, however, can be obtained except in combination with water or with a metallic oxide.

The *protoxide* or *manganous oxide* ( $\text{MnO}=71$ ) may be obtained easily by igniting manganous carbonate, or any of the higher oxides of the metal, in a current of hydrogen: it is of an olive-green colour, and unless it has been strongly heated, absorbs oxygen from the air; if ignited in the air it burns, and is converted into a brown superior oxide. It may be obtained as a white hydrate ( $\text{MnO}, \text{H}_2\text{O}$ ), by decomposing a manganous salt by any alkali, but it immediately begins to absorb oxygen from the air, and turns brown. It is soluble in ammonia, especially if the solution contain an ammoniacal salt. The protoxide, by its action upon acids, readily forms salts, which are of a pale rose colour; they are neutral to litmus.

*Sesquioxide, or Manganic oxide* ( $\text{Mn}_2\text{O}_3=158$ ); *Sp. Gr.* 4.82.—This oxide is found in its anhydrous form in acute square-based octohedra, constituting *braunite*; it occurs naturally in a hydrated state in *manganite* ( $\text{Mn}_2\text{O}_3, \text{H}_2\text{O}$ ; *sp. gr.* 4.35), which is of a blackish-brown colour, and forms brilliant right rhombic prismatic crystals. Manganic oxide may be obtained as a brown hydrate, by passing chlorine through manganous carbonate suspended in water, and afterwards removing the excess of the carbonate by means of diluted nitric acid. Sulphuric acid dissolves it slowly if a portion of the protoxide be present, and a deep-red solution is formed; hydrochloric acid in the cold also forms a soluble compound with it: if these solutions be heated they are decomposed, and a manganous salt is the result. When ignited, the sesquioxide loses one-eighth of its oxygen, and leaves the red oxide. The manganic salts or salts formed from the sesquioxide are isomorphous with those of alumina and ferric oxide. It appears to be the manganic oxide that imparts the violet colour to glass to which the black oxide has been added; and the colour of the amethyst is also said to be due to this oxide.

*Manganic dioxide, binoxide, deutoxide, or peroxide* ( $\text{MnO}_2=87$ ); *Sp. Gr.* 4.94; *Comp. in 100 parts*,<sup>†</sup> Mn, 63.22; O, 36.78.—This oxide is the black manganese of commerce and the *pyro-*

*lusite* of mineralogists; it is found in steel-grey rhombic prisms. *Psilomelane* is a black stalactitic or amorphous variety, frequently mixed with one of the lower oxides of the metal. *Varvicite* ( $\text{Mn}_2\text{O}_3, 2\text{MnO}_2, \text{H}_2\text{O}$ ; *sp. gr.* 4.53) is the name given to a hard lamellated crystalline hydrate, found by Phillips at Hartshill, in Warwickshire. *Wad* is also a hydrated dioxide of manganese, with a variable amount of water; it is in a less compact form than psilomelane, and is of a brown colour. Small quantities of cobalt and of the carbonates and nitrates of the metals of the earths are frequent constituents of these ores.

Dioxide of manganese is a good conductor of electricity, and is strongly electronegative in the voltaic circuit. When mixed with acids it furnishes a valuable oxidizing agent. When ignited, it gives off one-third of its oxygen, and the red oxide is left;  $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$ : if heated with concentrated sulphuric acid, half its oxygen escapes, and manganous sulphate is formed;  $2\text{MnO}_2 + 2\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + 2\text{H}_2\text{O} + \text{O}_2$ . With hydrochloric acid chlorine is abundantly evolved, and manganous chloride is left. Nitric acid has but little effect upon it. Dioxide of manganese is procured in a hydrated form as a reddish-brown powder ( $\text{MnO}_2, \text{H}_2\text{O}$ ) when potassic manganate or potassic permanganate is decomposed by an acid. When the red oxide is treated with nitric acid, a black hydrated dioxide is left, containing  $4\text{MnO}_2, \text{H}_2\text{O}$ . The same hydrate is probably formed on adding a solution of chloride of lime to a neutral solution of manganous sulphate or chloride.

(799) *Commercial Assay of Oxide of Manganese*.—The commercial value of black oxide of manganese depends upon the proportion of chlorine which a given weight of it will liberate when it is heated with hydrochloric acid. This quantity of chlorine varies much in different samples, and is dependent upon the proportion of oxygen which the oxide of manganese contains in excess of that which is necessary to its existence as protoxide. A convenient method of estimating this excess of oxygen is founded upon the circumstance that the black oxide of manganese is decomposed in the presence of oxalic acid and free sulphuric acid; manganous sulphate is formed, and all the excess of oxygen reacts upon the oxalic acid, and converts it into carbonic anhydride, which passes off with effervescence. If the mixture be weighed before the decomposition is effected, and again after it has been completed, the loss will indicate the amount of carbonic anhydride; and from this the available amount of oxygen is readily calculated. The reaction may be traced thus:  $\text{MnO}_2 + \text{H}_2\text{SO}_4 + \text{H}_2\text{C}_2\text{O}_4 = \text{MnSO}_4 + 2\text{CO}_2 + 2\text{H}_2\text{O}$ . Each atom of dioxide of manganese gives 2 atoms, or almost exactly its own weight, of carbonic anhydride.

The apparatus of Will and Fresenius (fig. 343, p. 401) is well adapted to the performance of this experiment: 5 grammes of the oxide of manganese to be tested, are reduced to an extremely fine powder, and mixed with 15 grammes of neutral potassic oxalate; the mixture is placed in the flask *a*, and about 60 cub. centimetres of water is added: the experiment is then proceeded with exactly as in the method already described for estimating carbonic anhydride in a carbonate



(578). The decomposition of the ore is known to be complete as soon as all the black particles have disappeared.

If the sample of oxide of manganese contain a carbonate of any of the earths, as may be readily ascertained by the effervescence which will be occasioned on moistening a portion of the oxide with diluted nitric acid, it will be necessary to remove this carbonate. This is easily done by washing the weighed portion in the flask itself with nitric acid diluted with from 16 to 20 parts of water; as soon as the effervescence has ceased, the acid liquid must be carefully poured off, and the flask filled up once or twice with distilled water; the oxide must be allowed to subside: in order to retain any suspended particles, the washings may be thrown upon a small filter, which is afterwards introduced into the flask, and the experiment is then proceeded with as usual.

The *Red oxide* ( $\text{Mn}_2\text{O}_3 = 229$ ); *Comp. in 100 parts*, Mn, 72.05; O, 27.95.—This oxide corresponds to the black oxide of iron; it is formed by igniting any of the oxides of manganese in the open air: it occurs native in *hausmannite* (*sp. gr.* 4.72) either massive or in four-sided pyramidal crystals of a black colour. The oxide is soluble in phosphoric and in sulphuric acid, but does not form definite salts with either of them.

(800) *Manganic acid* ( $\text{H}_2\text{MnO}_4 = 121$ ).—When equal weights of caustic potash and finely levigated dioxide of manganese are fused together, a substance is formed, which, when dissolved in a small quantity of water, has a green colour, but which, when largely diluted, becomes purple, and ultimately claret-coloured, whilst a precipitate of hydrated dioxide of manganese is deposited. This substance has, owing to these changes of colour, been long known under the name of *mineral chameleon*. The colouring material is potassic manganate,  $\text{K}_2\text{MnO}_4$ , which has a green colour: it is an unstable compound, and readily either parts with oxygen, or absorbs a larger amount of it, in the latter case forming a red compound; and hence these changes of colour are produced.

Manganic acid undergoes rapid spontaneous decomposition unless it be in combination with some powerful basyl. A tolerably stable manganate may be procured by heating finely powdered dioxide of manganese with its own weight of caustic potash, soda, or baryta. Béchamp heats an intimate mixture of 10 parts of finely powdered black oxide of manganese with 12 of caustic potash, dries it in an iron dish, and heats the porous residue to dull redness in an earthen retort, into the tubulure of which a green glass tube is luted; he then transmits a current of pure dry oxygen as long as it is absorbed. If the green mass thus obtained be treated with a small quantity of cold water, it is partially dissolved, forming a green solution, from which potassic manganate may be crystallized by evaporating it *in vacuo* over sulphuric acid. These crystals are isomorphous with the

corresponding sulphates and chromates. Potassic manganate ( $K_2MnO_4$ ) is anhydrous, and readily soluble in water. Sodid manganate is prepared on a large scale by Mr. Condry, by exposing a mixture of caustic soda and finely powdered oxide of manganese, to a dull red heat in shallow vessels, for 48 hours; 7 cwt. of oxide of manganese are mixed with the alkali obtained from  $1\frac{1}{2}$  ton of soda-ash. Manganic acid has a very intense colouring power: this fact enables us to detect manganese in very minute quantity before the blowpipe; the material supposed to contain it is fused upon platinum foil with a little potassic or sodic carbonate: if any trace of manganese be present, a green colour is imparted to the fused mass.

The *manganates* are very unstable; they are decomposed by boiling their solutions. A small quantity of any free acid changes the colour of their solutions from green to red, owing to the formation of a permanganate, and of a manganous salt: for instance,  $5K_2MnO_4 + 4H_2SO_4$ , gives  $4KMnO_4 + MnSO_4 + 3K_2SO_4 + 4H_2O$ . Organic matter also readily abstracts oxygen from them; their solutions must not even be filtered through paper. In the solid form they are readily decomposed by elevation of temperature, and oxygen is evolved; an excess of alkali renders the salt more stable. Sulphurous and hypophosphorous acids readily, and phosphorous acid more slowly, reduce the manganates to a manganous salt; sulphurous acid and potassic manganate, for example, produce the following result:—



(801) *Permanganic acid* ( $HMnO_4 = 120$ , or  $H_2Mn_2O_8$ ).—If a solution of potassic manganate be largely diluted with water, the colour changes from green to violet; the manganic acid passes to a higher state of oxidation, and potassic permanganate is formed.

This salt may be prepared by mixing intimately 4 parts of finely powdered dioxide of manganese with  $3\frac{1}{2}$  of potassic chlorate; 5 parts of caustic potash are dissolved in a small quantity of water, and added to the mixture, which is dried and reduced to powder, and then heated to dull redness for an hour in an earthen crucible. When cold, the mass is treated with water, and filtered through a funnel plugged with asbestos; the solution, after being neutralized with sulphuric acid, on evaporation yields beautiful red acicular crystals of potassic permanganate ( $KMnO_4 = 158$ ). If a solution of manganate, prepared by Béchamp's process, be decomposed by transmitting a current of carbonic acid until the green colour has been converted into red,

very fine crystals of the permanganate are obtained on evaporating the clear liquid after decantation from the precipitated oxide of manganese;  $3\text{K}_2\text{MnO}_4 + 2\text{CO}_2 = 2\text{KMnO}_4 + 2\text{K}_2\text{CO}_3 + \text{MnO}_2$ . The crystals of the permanganate are isomorphous with those of potassic perchlorate; they require about 16 parts of cold water for solution.

Potassic permanganate is in certain cases a useful oxidizing agent: it may be employed to detect the occurrence of sulphurous acid in solution in sulphuric or hydrochloric acid; sulphurous acid quickly deoxidizes it, and destroys its colour if present. Neutral solutions of the sulphides and the pentathionates quickly discharge the colour of a solution of potassic permanganate, and a similar effect is produced by acid solutions of the sulphites, hyposulphites, tetrathionates, sulphocyanides, and nitrites. The trithionates produce the same effect, but more slowly. Acidulated solutions of the mercurous, ferrous, stannous, and antimonious salts, and acid solutions of arsenites, likewise decolorize a solution of permanganate rapidly, whilst a manganous salt is formed. A solution of this salt constitutes a test-liquid which may be very usefully employed in many cases of volumetric analysis, as already exemplified in the instance of the ores of iron (778).

The *permanganates* are much more stable than the *manganates*; their solutions may be boiled without undergoing decomposition. Organic matter, however, combines with part of the oxygen contained in the acid, and reduces it first to manganic acid and then to the dioxide of the metal, which is precipitated in flocculi as a hydrate: their solutions, therefore, must not be filtered through paper, but through a funnel loosely plugged with asbestos. A dilute solution of the permanganate of known strength is employed to estimate the amount of oxidizable organic impurity in waters supplied for domestic use. When ignited, oxygen is given off, and a manganate is reproduced, which, if the heat be too great, is in turn decomposed with a further extrication of oxygen. Most of the permanganates are freely soluble in water; argentic permanganate is the least soluble of these salts. If concentrated solutions of potassic permanganate and argentic nitrate be mixed together, a red crystalline argentic permanganate is deposited. It may be employed for the preparation of the other permanganates; if it be levigated with water, and mixed with a solution of the chloride of the metal of which the permanganate is required, double decomposition occurs, and argentic chloride is formed, whilst the desired permanganate is obtained in

solution. In this way baric permanganate may be procured, and from it the permanganic acid may be obtained in solution, by the cautious addition of diluted sulphuric acid, so long as any precipitate is produced: on evaporation it may be obtained as a brown partially crystalline mass, which is very soluble in water: its solution is decomposed by mere elevation of temperature; at about  $104^{\circ}$  ( $40^{\circ}$  C.) hydrated dioxide of manganese is deposited, and oxygen gas escapes.

Condy has employed solutions of potassic manganate, and potassic permanganate, as disinfecting agents, for which purpose they are admirably adapted: the organic matter is rapidly and completely oxidized by their means, and as the solutions have no corrosive action, and no ill odour of their own, solutions of these salts form valuable local applications to foetid sores.

(802) *Manganous sulphide*, or *Protosulphide of manganese* ( $\text{MnS}, x\text{H}_2\text{O}$ ), is obtained as a yellowish-red hydrate, by precipitating a manganous salt by ammoniac hydrosulphide. The presence of traces of iron, cobalt, or nickel renders it black: it speedily becomes oxidized by exposure to the air. A crystalline sulphide may be obtained in black rhombic prisms, by heating the hydrated sesquioxide in the vapour of carbonic disulphide; native manganous sulphide is occasionally met with, as *manganese blende*, of a brownish-black or steel-grey colour, and feeble metallic lustre. The other sulphides of manganese have not been accurately examined.

(803) **CHLORIDES OF MANGANESE.**—Two chlorides of this metal may be obtained: manganous chloride,  $\text{MnCl}_2$ , and manganic chloride,  $\text{Mn}_2\text{Cl}_6$ .

*Manganous chloride* ( $\text{MnCl}_2, 4\text{H}_2\text{O} = 126 + 72$ ) *Sp. Gr.* 2.01. —This substance is obtained abundantly as a waste product in the preparation of chlorine, by acting on the black oxide of the metal: the chlorine escapes, and manganous chloride is dissolved.\* If this solution be evaporated to dryness,

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\* Various attempts have been made to economize the vast quantities of manganous chloride formed during the manufacture of chloride of lime. One of the most successful is the method employed by Mr. Dunlop. It consists in precipitating the manganese as carbonate, and roasting the carbonate at a temperature of about  $608^{\circ}$  ( $320^{\circ}$  C.). At Dieuze, in France, a process for the recovery of the waste manganese has been combined with one for turning the tank waste in the manufacture of sodic carbonate to account, by extracting from it a considerable proportion of its sulphur (p. 418), and the results are said to be very satisfactory.

The following is an outline of the method, given by Mr. J. L. Bell (*Chem. News*, Sept. 27, 1867):—

The acid liquor from the chlorine stills having been neutralized (by a process hereafter to be described), but still retaining the chlorides of manganese and iron, is mixed in suitable proportions with the soda waste. In a short time the metallic chlorides become converted into sulphides, by the action of the calcic sulphide, whilst soluble calcic chloride is formed, and much of it drains away;

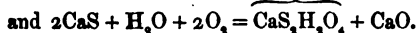
redissolved in water, and about one-fourth of its bulk be precipitated by means of sodic carbonate, an impure manganous carbonate is obtained. If this precipitate, after it has been well washed, is boiled with the remainder of the solution, the whole of the iron will be precipitated in the form of hydrated sesquioxide, while manganous oxide takes its place, and carbonic anhydride is expelled, leaving a solution of manganous chloride freed from all metallic impurities except cobalt and nickel. A still better process consists in concentrating a solution of the crude chloride by evaporation, to expel the excess of acid, and afterwards diluting with water. A current of sulphuretted hydrogen is transmitted, by which the iron is reduced to the state of ferrous salt; the manganese may then be obtained free from iron, nickel, and cobalt by suspending freshly precipitated manganous sulphide in water, and adding it to the liquid as long as the fresh portions of sulphide become blackened; the manganese displaces the other metals from their solution, and they are precipitated as black hydrated sulphides: for example,  $\text{FeCl}_2 + \text{MnS}, x \text{H}_2\text{O} = \text{MnCl}_2 + \text{FeS}, x \text{H}_2\text{O}$ . On evaporation the manganous chloride

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$\text{MnCl}_2 + \text{CaS} = \text{MnS} + \text{CaCl}_2$ . The solid residue is then removed from the tank and exposed to the atmosphere, turning it over from time to time to expose fresh surfaces to the air. The temperature of the mass rises gradually, owing to the absorption of oxygen, which must be moderated by keeping the materials moist. During this process the metallic sulphides are converted into hydrated oxides, whilst the sulphur at the moment of its liberation enters into combination with a portion of calcic sulphide, converting it into a persulphide: meantime the liberated oxides act upon a fresh portion of calcic sulphide, lime is set free, and the metals, whether iron or manganese, are reconverted into sulphides: these sulphides again become oxidized by further absorption of oxygen from the air, and the same cycle of changes is renewed as long as any unaltered calcic sulphide remains. A portion of calcic hyposulphite is formed at the same time. These changes may be illustrated by the following equations:—



Calcic hyposulphite.



The calcic polysulphide and hyposulphite are freely soluble, and are separated by lixiviation, forming a deep yellow liquid. The insoluble refuse is thus obtained destitute of offensive qualities, and it is stated may be kept without creating any nuisance in the neighbourhood. According to an analysis of it given by Mr. Bell, it contains a mixture of about 21 per cent. of lime, 66 of calcic sulphate, with a little carbonate, and about 9 per cent. of oxides of iron, manganese, and aluminum.

Meantime the sulphur is precipitated from the yellow liquor by the waste acid solution of manganous and ferric chlorides from the chlorine stills. This liquor is added until the precipitated sulphur begins to show a black tinge from precipitation of ferric sulphide, which happens as soon as all the free acid is

crystallizes in a tabular form with  $4\text{H}_2\text{O}$ . It is of a delicate pink colour and slightly deliquescent; by heat the anhydrous chloride may be procured, which is soluble in alcohol; from this solution it crystallizes with 4 atoms of alcohol ( $\text{MnCl}_2, 4\text{C}_2\text{H}_5\text{O}$ ).

*Manganic chloride* ( $\text{Mn}_2\text{Cl}_6$ ) may be obtained in solution by acting on manganic sesquioxide with cold hydrochloric acid: it is of a dark brown colour: it must be concentrated by evaporation *in vacuo*. It is converted by heat into  $2\text{MnCl}_2 + \text{Cl}_2$ .

An *oxychloride* (the *perchloride*,  $\text{Mn}_2\text{Cl}_8$ ? of Dumas) is obtained by dissolving potassic permanganate in oil of vitriol and adding fused sodic chloride, in small portions at a time; care is requisite in performing this operation, as if the temperature be allowed to rise too high the mixture sometimes explodes with violence: it is a greenish-yellow gas, which condenses at  $0^\circ$  ( $-18^\circ \text{C.}$ ) to a greenish-brown liquid. The fumes in a moist air assume a purple colour from the formation of permanganic acid: water decomposes it instantly, forming a red solution of permanganic and hydrochloric acids. It is probable that this compound is an oxychloride of the metal, somewhat analogous to the so-called chlorochromic acid (789).

*Fluorides* of manganese, corresponding to each of these chlorides, have been formed.

(804) MANGANOUS SULPHATE ( $\text{MnSO}_4, 5\text{H}_2\text{O} = 151 + 90$ ; *Sp. Gr. anhydr.* 3.1) is obtained for the use of the calico-printer, by

neutralized, the sulphur being precipitated in consequence of the reaction following:—



The precipitated sulphur is then removed from the liquid, and the greater portion of the liquor which it still retains is removed by pressure. It is then dried at a gentle heat and used for producing sulphuric acid.

The liquor thus rendered neutral still contains the iron and manganese, and is in a state fit for admixture with the soda waste as already described. From the surplus neutral liquors, after a sufficient quantity has been employed in the recovery of the sulphur, the manganese is obtained as follows:—The yellow sulphuretted lime liquor is added to the metallic chlorides, so long as it occasions a precipitate of black ferric sulphide, this is collected and dried: from the mode of its preparation it always contains free sulphur, and may be burned in kilns for making sulphuric acid; oxide of iron remaining.

The iron having been thus separated from the metallic solution a fresh quantity of the yellow liquor is added, and the whole of the manganese thrown down as sulphide, mixed with free sulphur. This precipitate, after drying, is also burned, and the sulphur converted into sulphuric acid. The burnt residue in this case consists of a mixture of the lower oxides of manganese with manganous sulphate. The oxides being free from iron are sold to the glassmakers, after the sulphate has been removed by washing. The concentrated solution of manganous sulphate thus obtained is mixed with an equivalent amount of sodic nitrate; and, when heated, the mixture becomes decomposed. Nitrous fumes are evolved, and are directed into the leaden chambers, whilst the residue consists of a mixture of sodic sulphate with oxide of manganese, containing from 60 to 70 per cent. of the binoxide:  $\text{MnSO}_4 + 2\text{NaNO}_3 = \text{Na}_2\text{SO}_4 + \text{MnO}_2 + 2\text{NO}_2$ . The sodic salt is removed by washing, after which both it and the oxide of manganese may be applied to their ordinary uses.

digesting the dioxide in diluted sulphuric acid, in order to remove the carbonates, then heating the oxide with oil of vitriol, evaporating to dryness, and gently igniting the residue to decompose the ferrous sulphate, which does not resist so high a temperature as manganous sulphate. On digesting the mass, after it has become cool, in water, the manganous sulphate is dissolved, and may be obtained in crystals by evaporation: it crystallizes below  $41^{\circ}$  ( $5^{\circ}$  C.) with  $7\text{H}_2\text{O}$  in efflorescent prisms; between  $45^{\circ}$  and  $68^{\circ}$  ( $7^{\circ}$  and  $20^{\circ}$  C.) with  $5\text{H}_2\text{O}$ ; and between  $68^{\circ}$  and  $86^{\circ}$  ( $20^{\circ}$  and  $30^{\circ}$  C.) with  $4\text{H}_2\text{O}$  (Brandes). It forms a double salt with potassic sulphate ( $\text{MnSO}_4, \text{K}_2\text{SO}_4, 6\text{H}_2\text{O}$ ), which is isomorphous with the corresponding magnesian sulphate.

*Manganic sulphate* cannot be obtained in crystals, but it was procured by Mitscherlich combined with potassic sulphate crystallized in octohedra ( $\text{KMn}'''2\text{SO}_4, 12\text{H}_2\text{O}$ ), and corresponding in form and composition with common alum.

(805) MANGANOUS CARBONATE ( $\text{MnCO}_3 = 115$ ).—The anhydrous carbonate forms the native *manganese spar*, and frequently accompanies spathic iron: the artificial carbonate may be obtained as a white hydrate ( $2\text{MnCO}_3, \text{H}_2\text{O}$ ) on precipitating manganous chloride by a carbonate of one of the alkali-metals: it becomes brownish by drying.

(806) CHARACTERS OF THE SALTS OF MANGANESE.—The salts formed from the *protoxide*, or manganous salts, are the only salts of manganese of importance: they are of a delicate rose colour, and have an astringent taste. With caustic *potash* and *soda* their solutions yield a white precipitate of hydrated protoxide, which absorbs oxygen rapidly, and becomes brown by exposure to the air. *Ammonia* gives a similar precipitate, which is soluble in excess of the ammoniacal liquid, especially when it contains ammoniac chloride; the solution absorbs oxygen quickly, and deposits a brown hydrated protosesquioxide. The *carbonates of the alkali-metals* give a white precipitate of manganous carbonate, soluble in ammoniac chloride. With *ammoniac hydrosulphide* a characteristic flesh-coloured hydrated manganous sulphide is formed, which is readily dissolved by hydrochloric and by nitric acid; it becomes brown by exposure to air. *Sulphuretted hydrogen* gives no precipitate in ordinary solutions of manganese; but a neutral solution of manganous acetate is partially precipitated by this gas. *Potassic ferrocyanide* gives in neutral solutions a white precipitate soluble in acids; in neutral solutions *potassic ferricyanide* produces a brown precipitate. Mr. Crum has pointed out an extremely delicate test of the presence of a manganous salt, provided that the solution is free from chlorides; the liquid must be mixed with diluted nitric acid, and

a little plumbic dioxide added : on boiling the mixture, the red colour of permanganic acid is produced by a trace of manganese which is too small to be otherwise recognized. *Before the blow-pipe*, when used on platinum wire or foil, with a little sodic carbonate, the compounds of manganese give a very characteristic bluish-green opaque bead : a bead of borax or of microcosmic salt becomes violet in the oxidizing flame, if manganese be present ; the colour disappears in the reducing flame.

(807) *Estimation of Manganese, and Separation from the Alkalies.*—Manganese is generally estimated in analysis in the form of the red oxide ( $\text{Mn}_2\text{O}_3$ ), which contains 72.05 per cent. of the metal. For this purpose it is precipitated from a boiling solution of its salts by potassic or sodic carbonate ; the precipitated carbonate is well washed, and then heated to redness, by which carbonic anhydride is expelled, and the red oxide is produced by absorption of oxygen from the air.

*Separation of Manganese from the Alkaline Earths.*—The solution must be rendered nearly neutral, and ammoniac hydro-sulphide added, which precipitates the manganese as sulphide : the sulphide must then be redissolved in hydrochloric acid, precipitated by potassic carbonate, and the manganese estimated, after ignition, as red oxide. It is apt, however, to retain some portions of the earths when thus separated. The oxide must therefore be again redissolved in hydrochloric acid ; ammoniac chloride must be added, and then a mixture of ammonia and ammoniac carbonate in excess, by which the manganese will be held in solution ; and if strontium, calcium, or barium be present, they will remain undissolved in the form of carbonates, which must be collected on a filter, weighed, and deducted from the weight of the oxide previously obtained.

*Separation from Zinc, Cadmium, Cobalt, and Nickel.*—The solution is mixed with potassic acetate in excess, to convert the metals into acetate, then sulphuretted hydrogen is transmitted ; the manganese remains in solution, whilst the other metals are precipitated as sulphides if the solution is only faintly acid. If cadmium alone is present, the addition of potassic acetate is unnecessary.

*Separation from Iron, Chromium, Uranium, Aluminum, and Glucinum.*—This is readily effected after converting the iron into a ferric salt and diluting the solution largely with water, by digesting it upon finely levigated baric carbonate. Manganese alone remains in the liquid, the other oxides being displaced by baryta. The excess of barium is removed by sulphuric acid, and the manganese precipitated by sodic carbonate.



Manganese is connected by isomorphous relations with a great number of the elementary bodies. Its protoxide is isomorphous with the oxides of the magnesian group: its sesquioxide is isomorphous with alumina and the ferric and chromic oxides. The manganates are isomorphous with the sulphates, and the permanganates with the perchlorates.

## CHAPTER XVII.

### GROUP VI.—CERTAIN METALS WHICH FORM ACIDS WITH OXYGEN.

Metal.	Sym- bol.	Atomic weight.	Solid atomic vol. H=1.	Specific heat.	Fusing point.		Specific gravity.	Electric conduc- tivity at 0° C.
					° C.	° F.		
{ Tin ...	Sn	118	16.20	0.0562	228	442	7.292	12.36
{ Titanium ...	Ti	50						
{ Molybdenum ...	Mo	96	10.56				8.62	
{ Tungsten ...	W	184	10.56	0.0334			17.60	
{ Vanadium ...	V	51.3						
{ Arsenic ...	As	75	12.96	0.0814			5.959	4.76
{ Antimony ...	Sb	122	18.16	0.0508	621	1150	6.71	4.62
{ Bismuth ...	Bi	210	21.34	0.0308	264	507	9.799	1.245

IN this list zirconium, thorium, columbium, and tantalum are omitted, because so little is known of them. The foregoing list of metals capable of yielding acids with oxygen is divisible into three natural families, which have little in common. (See p. 331.)

§ I. TIN (Stannum):  $\text{Sn}^{\text{IV}} = 118$ ; *Sp. Gr.* 7.292; *Fusing-pt.* 442° (227° 8 C.); *Dyad in Stannous salts, as*  $\text{SnCl}_2$ ; *Tetrad in Stannic salts, as*  $\text{SnCl}_4$ .

(808) THIS beautiful metal is one of those which have been longest known to man, as it is mentioned in the Books of Moses. Tin, however, is met with in but few localities. Its only ore of importance is the dioxide, or tin-stone, which occurs crystallized in prisms isomorphous with those of rutile. It is usually found in veins, running through primitive rocks of porphyry, granite, or clay-slate, and is generally mingled with the sulphides and arsenides of copper and iron, and frequently also with wolfram. The most celebrated tin mines are those of Cornwall, which were worked before the Roman invasion; they furnish annually upwards of 10,000 tons of the metal. The mines of Malacca also

yield a very pure tin ; the metal is likewise obtained to a smaller extent from Mexico. The tin-veins in Cornwall are frequently associated with those of copper, and they run almost invariably east and west. The tin ore is often met with in alluvial soils, whither it has been carried from its original position by the action of water. In this case the ore occurs in detached, rounded masses, and is very pure, constituting what is termed *stream tin*. The position of the veins is frequently traced by following the stream towards its source, up to the point where the ore ceases to be found ; a careful examination of the vicinity generally leads to the discovery of the vein.

(809) *Extraction of Metallic Tin*.—In order to extract the metal from the ore, it is subjected to a series of operations, some of which are of a mechanical and others of a chemical character. They may be classified thus:—

1.—*Stamping and washing*, to remove the earthy and lighter portions. 2.—*Roasting*, to decompose the pyrites and get rid of the arsenic and sulphur. 3.—*Washing*, to dissolve out cupric sulphate, and carry off the ferric oxide. 4.—*Reduction*, by which the tin is separated from the oxygen and the *gangue* or earthy matter. 5.—*Refining*, or liquation, and *boiling* with green wood.

1.—The purer portions of the ore are first picked out by hand ; the residue, consisting chiefly of tin-stone, with the earthy impurities of the matrix, mixed with arsenical copper and iron pyrites, passes to the stamping mill, where it is reduced to a coarse powder. This powder is then buddled and washed (529), to remove the lighter impurities.

2.—The heavier portion, however, still retains a considerable quantity of arsenical iron and copper pyrites. The next operation is intended to get rid of these substances ; with this view the washed ore is roasted in a reverberatory furnace until the arsenic and a good deal of the sulphur are expelled, and the ore becomes converted into yellowish-brown powder ; this process usually lasts about twelve hours. During this roasting, frequent stirring is necessary in order to expose fresh surfaces freely to the air. By this means the iron pyrites is decomposed, and is converted into sulphurous anhydride and ferric oxide ; the arsenic is expelled as arsenious anhydride, and the greater part of the sulphide of copper is converted into cupric sulphate ; this conversion is completed by exposing the mass in a moistened state to the air for some days.

3.—The cupric sulphate is then dissolved out by lixiviation ; after which the principal part of the ferric oxide, as it is much lighter than the stannic oxide, is got rid of by washing.

4.—The washed ore is now ready for reduction.\* In order to attain this object it is mixed with from one-fifth to one-eighth its weight of powdered anthracite or of charcoal, and with a small proportion of lime to facilitate the fusion of the siliceous gangue, which still remains mingled with the ore. The mixture having been rendered damp, for the purpose of preventing the finer particles from being carried away by the current of air, is introduced into the reducing furnace. This is a reverberatory furnace with a low arch or crown. The charge having been placed upon the hearth, the doors are closed up, and the heat is gradually raised for five or six hours; the stannic oxide is thus reduced by the carbon before the temperature rises high enough to cause the oxide to fuse with the silica, with which it would form an enamel difficult of reduction. Towards the end of the operation the heat is raised until it becomes very intense; the slags are thus rendered fluid, and the reduced metal subsides to the bottom, and is allowed to run off into cast-iron pans, from which it is ladled off into moulds; but the ingots so obtained are by no means pure.

5.—They are therefore next submitted to a process of *liquation*, which consists in heating the ingots to incipient fusion, upon the bed of a reverberatory furnace: the purer tin, being the more fusible portion, gradually melts out and leaves an alloy, which has a higher melting-point. This less fusible portion, when remelted, forms the inferior variety called *block tin*. The tin which has run out of the ingots is drawn off into a second pan in which the metal is gently heated, being kept in a state of fusion by a fire underneath; here it is agitated briskly by thrusting into the mass stakes soaked in water; the steam thus produced, as it bubbles up through the molten metal, carries the dust, slag, and other mechanical impurities to the surface. After this treatment has been continued for about three hours the metal is allowed to remain undisturbed for a couple of hours; it is then skimmed, ladled out, and cast into ingots for the market. The portion contained in the upper half of the pan is the purest, as owing to the low density of tin, and its tendency to separate from its alloys, it rises to the surface. The finest quality of the metal is frequently heated a second time to a temperature a little short of its melting-point;

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\* When much wolfram is contained in the ore it is sometimes fused with sodic carbonate before proceeding to the reduction; the tungstic acid is thus removed in the form of a soluble sodic tungstate, which is extracted by water, and is sometimes employed in calico-printing as a mordant; it has lately also been proposed to apply it to muslin dresses to prevent them from burning with flame, should they happen to take fire (618).

at this high temperature it becomes brittle, and, if allowed to fall from a height, it breaks into irregular prismatic fragments, which are known as *dropped* or *grain tin*. The splitting of the mass into these fragments is a rude guarantee of the purity of the metal, since impure tin does not become brittle in this manner.

On the Continent the stream tin is frequently reduced in small blast furnaces, termed by the French *fourneaux à manche*; the fuel used in this case is charcoal. The tin which is imported from Banca is almost chemically pure. English tin usually contains small quantities of arsenicum, copper, iron, and lead, and often traces of gold.

When required in a state of perfect purity, the metal may be obtained by means of voltaic action. For this purpose a concentrated solution of crude tin in hydrochloric acid may be placed in a beaker, and water cautiously poured in without disturbing the dense solution below. If a bar of tin be plunged into the liquid, beautiful foliated or prismatic crystals of pure tin are gradually deposited on the bar at the point of junction between the metallic solution and the water.

(810) *Properties*.—Tin is a white metal with a tinge of yellow, and a high metallic lustre. It is rather soft, and is very malleable, but is deficient in tenacity. At a temperature of about  $100^{\circ}\text{C}$ . its ductility is considerable, and it may then be easily drawn into wire. In a laminated state it is well known as *tin foil*. If a bar of tin be bent, it emits a creaking sound, a property which it possesses in common with cadmium; if bent several times in succession backwards and forwards, it becomes sensibly hot at the point of flexure. These effects depend upon a mechanical alteration of the relative position of its molecules, and their mutual friction. Tin, when handled, communicates a peculiar odour to the fingers. It is a tolerably good conductor both of heat and electricity. It fuses at  $442^{\circ}$  ( $227^{\circ}\text{--}8^{\circ}\text{C}$ .), according to Crichton, or  $451^{\circ}\text{--}4$  ( $233^{\circ}\text{C}$ .), (Person), but is not sensibly volatilized in the furnace. It may be obtained in crystals by slow cooling after fusion. Tin is but slowly tarnished by exposure to the air and moisture at ordinary temperatures, but if heated to redness in a current of steam, or if exposed to the air at a high temperature, it becomes rapidly converted into the dioxide and burns with a brilliant white light. Nitric acid of sp. gr. 1.52 does not attack tin, but if diluted to 1.3 it acts upon it violently, and produces an insoluble hydrated dioxide of the metal known as metastannic acid; at the same time, owing to the decomposition of water, a considerable quantity of ammonia is formed, which enters into combination with

the excess of nitric acid. Strong hydrochloric acid, when heated upon tin, dissolves it gradually with extrication of hydrogen. Aqua regia, if not too concentrated, dissolves the metal and converts it into the tetrachloride. Diluted sulphuric acid is without action on the metal in the cold; but if the concentrated acid be boiled upon it, the tin becomes converted into stannic sulphate, and globules of sulphur are separated, while sulphurous anhydride escapes: the tin appears in this case to be dissolved as stannous sulphate, which is oxidized to stannic sulphate at the expense of the sulphurous acid, and sulphur is deposited;  $\text{Sn} + 2\text{H}_2\text{SO}_4$  yielding  $\text{Sn}''\text{SO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$ ; and  $2\text{Sn}''\text{SO}_4 + \text{SO}_2 + 2\text{H}_2\text{SO}_4$  furnish  $2(\text{Sn}''2\text{SO}_4) + \text{S} + 2\text{H}_2\text{O}$ . Potassic and sodic hydrates act upon tin at high temperatures, hydrogen being evolved, whilst a soluble metastannate of the alkali-metal is formed. Tin combines readily with sulphur, phosphorus, chlorine, and bromine, if heated with them.

Owing to its brilliancy, and its power of resisting ordinary atmospheric changes, tin is largely employed as a coating upon other more abundant but more oxidizable metals, to protect them during use. Iron and copper are especially adapted to the operation of tinning. In India, tin is applied instead of silver to steel and iron articles by way of ornament; the tin is melted, and while still liquid is agitated in a box till it has become solid; the fine powder thus procured is separated, by suspension in water, from the coarser particles, and is made into a thin paste with glue; it is then applied in the desired pattern; when perfectly dry it is burnished, and afterwards varnished; its brilliancy is thus preserved unchanged.

(811) *Tin-Plate*.—The ordinary process of tinning iron differs from the foregoing one, and is far more important in its economical results. In tin-plate an actual alloy of the two metals is formed upon the surface of the iron, the external surface being pure tin.

For the manufacture of tin-plate, the best charcoal iron is required. After the iron has been rolled and cut into sheets of suitable thickness and size, its surface is made chemically clean. For this purpose the sheets are immersed for four or five minutes in a mixture of sulphuric acid and water; after which they are raised to a red heat in a reverberatory furnace; they are then withdrawn, allowed to cool, and hammered flat. In order to detach from them all the scales of oxide, they are passed between polished rollers, and as they emerge they are plunged one by one into a mixture of bran and water which has become sour by exposure to the air; here they remain for some hours, and are thence transferred to a vessel containing a mixture of diluted sulphuric and hydrochloric acids; lastly, they are scoured with bran, and plunged into pure water or lime-water, in which last, if the surface be clean on immersion, they may remain for

any length of time without rusting: these preliminary steps are necessary in order to secure a clean surface, as the tin will not adhere to an oxidated or even a dusty plate. In some works, the plates, after they have been scoured, are further cleaned with hydrochloric acid holding zinc in solution, and then dipped into the melted tin in the manner about to be described.

The plates having been prepared by either of the foregoing processes are next plunged one by one into a large vessel of melted tallow free from salt, and after remaining there for an hour they are immersed in the bath of melted tin, which is preserved from oxidation by a stratum of grease three or four inches (8 or 10<sup>cm.</sup>) thick. Here they remain for about an hour and a half; they are then withdrawn and allowed to drain. After this they are plunged into a second bath of pure tin, and the excess of tin is removed by again heating them in a bath of tallow: the tin melts and runs down to the lower edge of the plate; when cool, this thickened margin is finally reduced by dipping the edge of the plate once more into tin kept at a temperature much above its melting-point; the heat quickly fuses the superfluous metal, which is then detached by giving the plate a sharp blow. Tin-plate is sometimes made to exhibit a beautiful crystalline appearance, known under the term *moirée métallique*. A mixture of 2 parts of nitric acid, with 2 of hydrochloric acid, is made with 4 of water: the tin-plate is gently heated, and the liquid spread evenly over with a sponge; the crystals gradually appear. The plate is then plunged into water, dried quickly, and varnished. Different coloured varnishes are used to vary the effects.

Tinning of copper is the same in principle, but is a simpler operation than the tinning of iron: the surface of the metal is rendered clean by rubbing it, while heated, with sal ammoniac; when quite bright the copper is sprinkled with a little rosin to prevent oxidation, and melted tin is then poured on and spread over the surface with tow by the workman, who keeps the article constantly at a high temperature; the superfluous tin is wiped off with the tow. The addition to the tin of one-fourth of its weight of lead renders the operation more easy, as the alloy is more perfectly liquefied. Pins, which are made of brass wire, are tinned by boiling them for a few minutes with a solution containing 1 part of cream of tartar, 2 parts of alum, and 2 of common salt in 12 parts of water, with a quantity of granulated tin: in the course of a few minutes a brilliant, white, closely adhering coat of tin is deposited upon the surface of the pins.

(812) *The alloys of tin* which are employed in the arts are numerous. *Britannia metal* is a white alloy which is a good deal used for making teapots and spoons of a low price; it consists of equal parts of brass, tin, antimony, and bismuth. *Pewter* is another alloy of this description; both of these possess considerable malleability, pewter being intermediate in hardness between lead and Britannia metal. The best pewter consists of 4 parts of tin, and 1 of lead. Another alloy, which is intermediate in properties between pewter and Britannia metal, is called *Queen's metal*; it is used for the manufacture of teapots and common spoons. It consists of 9 parts of tin, 1 part of antimony, 1 of bismuth, and 1 of lead. *Plumber's solder* is an alloy of tin and lead which is more fusible than pure lead: *fine solder* consists of 2 parts tin and 1 of lead; *common solder* of equal parts of lead and tin; and *coarse solder* is composed of 2

of lead to 1 of tin. Lead and tin may be melted together in all proportions, and notwithstanding their difference in density, they do not separate when the fused mixture is allowed to cool slowly (Matthiessen). The same is true also of the alloy of tin and zinc; if the two metals be fused together in equal proportions, the result forms a hard, white alloy nearly as tough as brass.

Tin forms several important alloys with copper. *Speculum metal*, used for the mirrors of reflecting telescopes, consists of 1 part tin and 2 copper, or  $(\text{Cu}_2\text{Sn})$ : it is of a steel-white colour, extremely hard, brittle, and susceptible of a high polish. The proportions of the constituents of speculum metal recommended by different authorities vary, and sometimes a small quantity of arsenic is added to the alloy. *Bell metal* consists of about 78 of copper and 22 of tin, or  $(\text{Cu}_2\text{Sn})$ : sometimes a mixture of zinc and lead is substituted for a part of the tin. *Gun metal* contains only 9 or 10 per cent. of tin. *Bronze* contains less tin than bell-metal, with usually an addition of 3 or 4 per cent. of zinc. The bronze used for coin consists of 95 parts of copper, 4 of tin, and 1 of zinc. Bronze admits of a peculiar kind of tempering. If it be annealed, and allowed to cool slowly, it becomes hard, brittle, and elastic; but if cooled suddenly, it may be hammered, and worked at the lathe; this property is taken advantage of in the manufacture of articles with this alloy; they are wrought in the soft state, and are afterwards hardened by annealing. The effect of sudden cooling upon bronze is therefore just the reverse of that which is produced by it upon steel. These alloys of copper and tin are much harder than copper itself, and considerably more fusible. The melting-point of copper, according to Daniell, is  $1996^\circ$  ( $1091^\circ\cdot 1$  C.); but an alloy of tin and copper containing 6·6 per cent. of tin, fused at  $1690^\circ$  ( $921^\circ\cdot 1$  C.); and 1 with 12·3 per cent. of tin, at  $1534^\circ$  ( $834^\circ\cdot 4$  C.). These alloys have a specific gravity greater than the mean of that of the metals which enter into their composition. They resist oxidation in the air more completely than copper.

An inconvenience in the use of the alloys of copper and tin arises from the circumstance, that, when melted, the two metals, owing to their difference in density, have a tendency to separate from each other, even after they have been well incorporated: the tin accumulates in the upper portions of the melted mass, where it forms a more fusible alloy. It is therefore very difficult in large castings to obtain a mass of metal the composition of which is uniform throughout.

The *amalgam of tin and mercury* is employed for the silvering of mirrors.

In order to apply it to the glass, a sheet of tinfoil is spread evenly upon a smooth slab of stone, which forms the top of a table carefully levelled, and surrounded by a groove, for the reception of the superfluous mercury. Clean mercury is poured upon the tinfoil, and spread uniformly over it with a roll of flannel; more mercury is then poured on till it forms a fluid layer of the thickness of about half-a-crown; the surface is cleared of impurities by passing a linen cloth lightly over it; the plate of glass is carefully dried, and its edge being made to dip below the surface of the mercury, is pushed forward cautiously; all bubbles of air are thus excluded as it glides over and adheres to the surface of the amalgam. The plate is then covered with flannel, weights are placed upon the glass, and the stone is gently inclined so as to allow the excess of mercury to drain off; at the end of 24 hours it is placed upon a wooden table, the inclination of which is increased from day to day until the mirror assumes a vertical position: in about a month it is sufficiently drained to allow the mirror to be framed. The amalgam usually contains about 4 parts of tin to 1 part of mercury.

Several of the compounds of tin are employed in the arts. The dioxide is used to some extent in the preparation of enamels, and both the chlorides of tin are substances of great importance to the dyer and the calico-printer.

(813) OXIDES OF TIN.—With oxygen, tin forms two principal compounds, the protoxide or stannous oxide and the dioxide or stannic oxide, besides some intermediate oxides of minor importance.

*Stannous oxide, or Protoxide of tin* ( $\text{SnO} = 134$ ), is obtained as a white hydrate ( $2\text{SnO}, \text{H}_2\text{O}$ ), by pouring a solution of stannous chloride into one of sodic or potassic carbonate in excess; the carbonic anhydride escapes with effervescence. When moist, this hydrate absorbs oxygen from the air, but not when dry. By ignition in closed vessels filled with nitrogen or with carbonic anhydride it becomes anhydrous. The anhydrous protoxide may also be obtained by decomposing stannous oxalate by heat in closed vessels. If heated in the open air it glows, and is converted into the dioxide. If the hydrated protoxide be boiled with a solution of potash in excess, it is dissolved, and in a few days metallic tin is separated, stannic oxide remaining in solution. If boiled with a weak solution of potash, in quantity insufficient to dissolve the protoxide, it becomes anhydrous, and is converted into a mass of black crystalline needles; these needles when heated decrepitate powerfully, increase in bulk, and are converted into an olive-brown powder. By evaporating down a solution of sal ammoniac containing hydrated stannous oxide in suspension until the sal ammoniac begins to crystallize, the oxide becomes anhydrous and assumes a brilliant scarlet colour, which, however, by friction disappears, and becomes brown. Hydrated stannous oxide is readily dissolved by acids, but the anhydrous oxide is more slowly acted upon by them.



(814) *Stannic oxide*, or *Binoxide of tin* ( $\text{SnO}_2 = 150$ ); *Sp. Gr.* 6.95; *Comp. in 100 parts*, Sn, 78.66; O, 21.34.—This oxide occurs native in the anhydrous form as *tin-stone*, and constitutes the only ore of tin that is worked. It is met with crystallized in square prisms, which are hard enough to scratch glass; they have usually a brown colour, owing to the presence of ferric oxide or of manganic dioxide. It is insoluble in acids, but if heated with an alkali, it enters into combination with it, and forms a soluble compound.

In its hydrated condition dioxide of tin has the characters of an acid, and forms two remarkable varieties which have been termed respectively metastannic and stannic acids (Fremy, *Ann. de Chimie*, III. xxiii. 393). Like the metaphosphoric and phosphoric acids, they require each a different amount of base for saturation, the stannic acid combining with the greatest proportion of base.

*Metastannic acid* ( $\text{H}_2\text{Sn}_5\text{O}_{11} \cdot 4\text{H}_2\text{O}$ ) is readily procured by treating metallic tin with nitric acid; violent action, attended with extrication of nitrous fumes, occurs, and the tin is converted into a white, crystalline, insoluble mass, which is hydrated metastannic acid; after washing it with cold water, the acid, when dried in air, consists of ( $\text{Sn}_5\text{O}_{10} \cdot 10\text{H}_2\text{O}$ ; Fremy). In this state it reddens litmus-paper; when dried at  $100^\circ \text{C}$ . it loses half its water; at  $266^\circ$  ( $130^\circ \text{C}$ .) it loses an additional atom of water, and by ignition becomes anhydrous, and of a pale buff colour: in this form it possesses the properties of the native dioxide, and constitutes the *putty powder* employed for polishing plate; it is also largely used for giving whiteness and opacity to enamels.

In its hydrated condition, metastannic acid is insoluble in nitric acid; concentrated sulphuric acid, when heated with it, dissolves it freely and forms a compound soluble both in water and in alcohol; by boiling the solution it is decomposed, and the two acids are separated. Hydrochloric acid combines with it, but does not dissolve it; the compound is soluble in pure water, but is reprecipitated on the addition of acid in excess, or on boiling the solution. Metastannic acid is freely soluble in solutions of potash and of soda, as well as in solutions of their carbonates, but it is not dissolved by ammonia, unless recently precipitated from a cold solution of its salts by the addition of an acid; the precipitate is not soluble in ammonia after it has been boiled. The metastannates are not crystallizable, and are precipitated by adding caustic potash to their aqueous solution; the granular precipitate may be drained upon a tile, and dried at

$266^{\circ}$  ( $130^{\circ}$  C.); their normal formula is  $M'_2\text{Sn}_5\text{O}_{11}$  with usually  $4\text{H}_2\text{O}$ .

The potassium salt has a strongly alkaline reaction; it consists of ( $\text{K}_2\text{Sn}_5\text{O}_{11}\cdot 4\text{H}_2\text{O}$ ). The metastannates of the alkalis can only exist in the hydrated condition; if strongly heated they are decomposed and become insoluble; when the residue, after ignition, is treated with water, metastannic acid is left, whilst the alkali is dissolved. Metastannic acid may be recognized by the beautiful golden-yellow colour which it yields when its hydrate is moistened with a solution of stannous chloride, owing to the formation of stannous metastannate ( $\text{Sn}_2\text{Sn}_5\text{O}_{11}\cdot 4\text{H}_2\text{O}$ ). The only metastannates which are soluble are those of potassium and sodium; they are precipitated in the gelatinous state from their solutions by the addition of almost any of the neutral salts of sodium, potassium, or ammonium.

(815) *Stannic Acid* ( $\text{H}_2\text{SnO}_3$ ).—This variety of the hydrated stannic oxide may be procured by precipitating a solution of stannic chloride by ammonia, or still better by adding to the solution of the tetrachloride a quantity of an insoluble carbonate, such as chalk or baric carbonate, insufficient for its entire decomposition; it is thus separated as a gelatinous precipitate, which may be readily washed clean: when dried *in vacuo*, the composition of the hydrate is ( $\text{H}_2\text{SnO}_3$ ). In this state it is freely soluble in hydrochloric acid, with which it reproduces stannic chloride; it is also soluble even in diluted sulphuric acid, but the stannic acid is separated on boiling. Nitric acid dissolves it freely. Stannic acid is soluble in the cold in solutions of potash and of soda, but not in ammonia; by a heat of  $284^{\circ}$  ( $140^{\circ}$  C.) it is converted into metastannic acid. In combination with the alkalis it forms compounds which crystallize readily, especially from solutions which contain an excess of alkali. The general formula is  $M'_2\text{SnO}_3$ .

The soluble stannates have a powerfully alkaline reaction; they absorb carbonic acid from the air when in solution, and are precipitated by solutions of most of the salts of potassium, sodium, and ammonium.

*Potassic stannate* ( $\text{K}_2\text{SnO}_3\cdot 3\text{H}_2\text{O}$ ; Moberg) is easily prepared by heating any form of stannic oxide with excess of caustic potash; on dissolving and evaporating the product, transparent oblique rhombic prisms are formed. When heated to redness, potassic stannate may be rendered anhydrous. *Sodic stannate* ( $\text{Na}_2\text{SnO}_3\cdot 3\text{H}_2\text{O}$ ) may be prepared in a manner similar to that employed for potassic stannate. It crystallizes with facility in six-sided tables, when a solution saturated at about  $104^{\circ}$  ( $40^{\circ}$  C.) is heated to the boiling-point, as it is more soluble in cold than in hot water. This stannate is now largely prepared as a mordant for the use of the dyer and calico-printer. It forms the basis of what is technically known as *tin-prepare liquor*. Copper is quickly tinned by a solution of this salt.

*Sesquioxide of tin, or Stannous stannate* ( $\text{Sn}_2\text{O}_3$ , or  $\text{SnO}\cdot\text{SnO}_2$ ), may be prepared as a slimy grey hydrate, soluble in ammonia, by boiling pure hydrated ferric oxide with a solution of stannous chloride; ferrous chloride remains in

solution,  $2\text{SnCl}_2 + \text{Fe}_2\text{O}_3 = 2\text{FeCl}_3 + \text{SnO}, \text{SnO}_2$ . It is soluble in hydrochloric acid and also in ammonia, which latter reaction seems to indicate that it is really a distinct oxide; the hydrochloric solution gives a purple precipitate with salts of gold.

(816) THE SULPHIDES OF TIN are three in number,—the protosulphide, the disulphide, and the sesquisulphide: the latter is unimportant.

*Stannous sulphide*, or *Protosulphide of tin* ( $\text{SnS} = 150$ ), may be procured by fusing the metal with sulphur, when it forms a bluish-grey crystalline mass, easily dissolved by melted tin; it may also be obtained by passing sulphuretted hydrogen through a stannous salt in solution, when it falls as a chocolate-brown hydrate. It is soluble in solution of ammoniac disulphide, and in the sulphides of the alkali-metals, if they contain an excess of sulphur. Stannous sulphide combines with the sulphides of the electronegative metals, such as arsenicum and antimony. Hydrochloric acid dissolves it with extrication of sulphuretted hydrogen.

The *Sesquisulphide* ( $\text{Sn}_2\text{S}_3$ ) may be prepared by mixing stannous sulphide with one-third of its weight of sulphur, and heating to dull redness; it is only partially soluble in hydrochloric acid.

*Stannic sulphide*, or *Disulphide of tin* ( $\text{SnS}_2 = 182$ ), is known as *mosaic gold*; it forms a beautiful yellow flaky compound, which is obtained by preparing an amalgam of 12 parts of tin and 6 of mercury: this is reduced to powder and mixed with 7 parts of sublimed sulphur and 6 of sal ammoniac. The mixture is introduced into a flask with a long neck, and is heated gently so long as any smell of sulphuretted hydrogen is perceptible; the temperature is then raised to low redness; calomel and cinnabar are sublimed, and a scaly mass of stannic sulphide remains. If the heat be pushed too far, part of the sulphur is expelled, and the operation fails: the sal ammoniac appears by its volatilization to moderate the heat produced during the sulphuration of the tin, which would otherwise rise so high as to decompose the disulphide, and it mechanically preserves the requisite flaky structure of the compound. Stannic sulphide is used in the arts to imitate bronze. Aqua regia is the only acid that decomposes it, but it is readily soluble in the alkalis. A hydrated stannic sulphide, of a dingy yellow, is produced by passing sulphuretted hydrogen through a solution of one of the stannic salts. This hydrate is readily dissolved by ammoniac hydrosulphide, with evolution of sulphuretted hydrogen: it is also soluble in the alkalis, and in hot hydrochloric acid. With disodic sulphide it forms a salt which may be obtained in yellow crystals, consisting of  $2\text{Na}_2\text{S}, \text{SnS}_2, 12\text{H}_2\text{O}$ .

Stannic sulphide fuses when chlorine is passed over it; 6 atoms of the gas

are absorbed, without the aid of heat, by each atom of disulphide, and a yellow crystalline compound is obtained which may be considered as a combination of 1 atom of stannic chloride with 2 atoms of sulphur tetrachloride;  $\text{SnCl}_4, 2\text{SCl}_4$ .

(817) CHLORIDES OF TIN.—Tin forms with chlorine two compounds,  $\text{SnCl}_2$  and  $\text{SnCl}_4$ , formerly termed the chloride and bichloride of the metal, but now distinguished as *stannous chloride* and *stannic chloride*.

*Stannous chloride*, formerly *Protochloride of tin* ( $\text{SnCl}_2 = 189$ ).—The hydrate of this salt may be obtained by dissolving tin in hydrochloric acid. This solution is usually effected on the large scale in copper vessels, since the voltaic opposition of the two metals favours the solution of the tin: on evaporating the liquid till it crystallizes, prismatic needles are formed ( $\text{SnCl}_2, 2\text{H}_2\text{O}$ ; *sp. gr.* 2.710); by a heat of  $100^\circ \text{C}$ . it may be rendered anhydrous, but it generally loses a portion of hydrochloric acid at the same time. Stannous chloride is decomposed if mixed with a large quantity of water, hydrochloric acid remains in solution, and a white hydrated oxychloride ( $\text{SnCl}_2, \text{SnO}, 2\text{H}_2\text{O}$ ) subsides. When exposed to the air, in crystals or in solution, stannous chloride absorbs oxygen and forms a mixture of stannic chloride and oxychloride. Stannous chloride has a strong attraction both for chlorine and for oxygen; it therefore acts as a powerful reducing agent. For example, it deoxidizes completely the salts of mercury, of silver, and of gold. Advantage is sometimes taken of this circumstance in the analytical determination of the quantity of mercury, since all the salts of mercury, when boiled with stannous chloride, are decomposed, and yield their mercury in a metallic form. Sulphurous acid is likewise deprived by it of its oxygen, producing a yellow precipitate of stannic sulphide when mixed with a solution of the salt. Stannous chloride reduces the metallic acids in the salts of chromic, tungstic, molybdic, arsenic, antimonie, and manganic acids to a lower state of oxidation; it also converts the ferric into ferrous salts, and the cupric into cupreous salts. Stannous chloride is extensively employed as a mordant by the dyer and calico-printer, under the name of *salts of tin*, and they also use it for deoxidizing indigo and the peroxides of iron and manganese.\* It forms double chlorides with

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\* The proportion of stannous chloride available for this purpose in any commercial sample may be determined by Penny's method:—A solution of a weighed quantity of stannous chloride in hydrochloric acid is taken, and a standard solution of potassic anhydro-chromate (bichromate) is added until a drop of the liquid when mixed with plumbic acetate gives a yellow precipitate, showing that the chromic acid is no longer reduced:  $3\text{SnCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} = 3\text{SnCl}_4 + 2\text{KCl} + \text{Cr}_2\text{Cl}_6 + 7\text{H}_2\text{O}$ .

many of the chlorides of the metals of the alkalies and alkaline earths; these double salts are capable of crystallization.

The anhydrous stannous chloride, or *butter of tin*, may be procured by distilling a mixture of equal weights of tin filings and corrosive sublimate;  $\text{HgCl}_2 + \text{Sn} = \text{SnCl}_2 + \text{Hg}$ : it remains behind as a grey brilliant mass with a vitreous fracture; at a full red heat it may be distilled. On passing a current of chlorine over it, heat and light are evolved, and stannic chloride is formed.

(818) STANNIC CHLORIDE, or *Tetrachloride of tin*, formerly *Bichloride of tin* ( $\text{SnCl}_4 = 260$ ); *Rel. wt.* 130; *Sp. Gr. of vapour*, 9.2; *of liquid*, 2.267 at  $32^\circ$  ( $0^\circ$  C.); *Mol. Vol.*  ; *Boiling-pt.*  $239^\circ.5$  ( $115^\circ.3$  C.).—This compound may be prepared either by passing dry chlorine over melted tin, or by mixing 4 parts of corrosive sublimate with 1 part of tin filings: on the application of heat a colourless liquid distils;  $2\text{HgCl}_2 + \text{Sn}$  yielding  $\text{SnCl}_4 + 2\text{Hg}$ . It emits dense white fumes when exposed to the air: when mixed with water, intense heat is evolved, and a hydrate is formed; this compound crystallizes in rhombohedra ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ; Lewy) when it is allowed to form spontaneously, by attracting moisture from the air; *in vacuo* it loses  $3\text{H}_2\text{O}$ : but though freely soluble in a small quantity of water, copious dilution causes the precipitation of hydrated stannic acid, and hydrochloric acid is set free. Stannic chloride is readily soluble in water acidulated with hydrochloric acid. When its aqueous solution is mixed with a solution of the sulphate of one of the alkali-metals, hydrated stannic oxide is precipitated;  $\text{SnCl}_4 + 4\text{H}_2\text{O} + 4\text{Na}_2\text{SO}_4$  becoming  $\text{SnO}_2 \cdot 2\text{H}_2\text{O} + 4\text{NaCl} + 4\text{NaHSO}_4$ , acid sulphate of the alkali-metal remaining in solution. Stannic chloride forms numerous double salts with the soluble chlorides; the compound with potassic chloride crystallizes in anhydrous octohedra,  $2\text{KCl} \cdot \text{SnCl}_4$ ; a similar constitution holds in the corresponding ammoniacal salt ( $2\text{H}_4\text{NCl} \cdot \text{SnCl}_4$ ), which is the *pink salt* of the dyer. An impure stannic chloride is largely used by the dyers under the name of nitromuriate of tin, or *composition*; it is generally prepared by dissolving tin at a gentle heat in a mixture of nitric acid and sal ammoniac.

The other salts of tin are unimportant. Stannic sulphate ( $\text{Sn}_2\text{SO}_4$ ) is soluble in water strongly acidulated by sulphuric acid, but is precipitated to a large extent on copious dilution with water.

(819) CHARACTERS OF THE SALTS OF TIN.—Tin forms two series of salts, the salts formed from the protoxide and the salts formed from the dioxide: stannic chloride is the only salt of the latter class that has been minutely examined.

1.—The *stannous salts*, or *protosalts of tin*, are nearly colour-

less; with the exception of the chloride, they are not often prepared: they have a powerfully astringent taste; when in solution they absorb oxygen rapidly from the air; when largely diluted with water the solution becomes milky, but it is rendered clear by a small excess of hydrochloric acid. The hydrates of the *fixed alkalies* produce a white precipitate of hydrated stannous oxide, which is soluble in excess of the alkali, but on boiling, part of the oxide is deposited as a black crystalline powder. *Ammonia* gives a white hydrated stannous oxide, but the precipitate is not redissolved by an excess of ammonia. The *carbonates of the alkali-metals* give a similar precipitate, whilst carbonic anhydride escapes with effervescence. A very characteristic reaction is the production, with *sulphuretted hydrogen*, of a chocolate-brown precipitate of hydrated stannous sulphide. With *ammonic hydrosulphide* a similar precipitate is formed, which is soluble in excess of the precipitant and in the sulphides of the alkali-metals. With a dilute solution of *auric chloride*, they give, if used in excess, a brown precipitate of reduced gold; in smaller quantity, they yield a beautiful purple precipitate, the purple of Cassius. *Potassic ferrocyanide* gives a white precipitate, soluble in hydrochloric acid.

2.—The *stannic salts*\* are found to give with the *caustic alkalies* a white precipitate, soluble in excess of the alkalies, and this solution yields no precipitate when it is boiled. *Carbonates of the alkali-metals* give a white hydrated dioxide with escape of carbonic anhydride: the precipitate is insoluble in excess of the alkaline salt. *Sulphuretted hydrogen* and *ammonic hydrosulphide* both produce a dirty yellow precipitate of hydrated stannic sulphide, which is soluble in excess of the precipitant, as well as in the sulphides of the alkali-metals, and in the caustic alkalies.

All the compounds of tin *before the blowpipe*, in the reducing flame on charcoal, give with sodic carbonate white malleable globules of the reduced metal.

(820) *Estimation of Tin, and Separation from the foregoing Metals*.—Tin is estimated in the form of the anhydrous dioxide; 100 parts of which contain 78·66 of the metal.

The separation of tin from all the metals hitherto described, with the exception of cadmium, is effected by means of sulphuretted hydrogen, which precipitates none of these metals from their solutions in the mineral acids. The mixed sulphides of tin and cadmium may be at once evaporated to dryness with nitric acid: on treating the residue with water, cadmic nitrate will be dissolved,

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\* The presence of tartaric acid in some cases interferes with these reactions.

and the insoluble metastannic acid will remain. The cadmic sulphide is also easily separated from the sulphides of tin by ammoniacal disulphide, which dissolves the sulphides of tin and leaves the cadmic sulphide. Both the sulphides of tin, by ignition in a current of air, are gradually converted into the stannic oxide: this change may be accelerated by moistening them with nitric acid.

Tin may also be separated from all metals with the exception of antimony, arsenicum (and lead if sulphuric acid be present), by evaporating the solution nearly to dryness with nitric acid, and washing the residue with water strongly acidulated with nitric acid. The tin remains as metastannic acid, and by ignition furnishes the anhydrous dioxide.

## § II. TITANIUM: (Ti=50). *Tetrad, as in $\text{TiCl}_4$ .*

(821) TITANIUM is a comparatively rare metal, which presents considerable analogy with tin. It was discovered by Gregor as a constituent of menaccanite, in the year 1791. Its principal ores are titaniferous iron, and rutile, anatase, and brookite, which are three different forms of titanic anhydride, coloured by variable quantities of the oxides of iron, manganese, and chromium. Many clays also contain small quantities of titanic acid. When titanic anhydride is intensely heated with charcoal, it is reduced, but is not fused. A remarkable compound of the metal is frequently found, in the form of copper-coloured cubic crystals, adhering to the slags of the Welsh and other iron furnaces. These crystals are hard enough to scratch agate; they have a specific gravity of 5.3. No acid, except a mixture of nitric and hydrofluoric acids, has any action upon them, but they are oxidized by fusion with nitre, or by ignition in a current of oxygen: they are volatile at an extremely high temperature. These crystals were supposed by Wollaston to be metallic titanium, but Wöhler showed that they consist of a combination of cyanide with nitride of titanium; they contain 18 per cent. of nitrogen, and 4 of carbon, having a formula  $(\text{TiCy}_{23}\text{Ti}_3\text{N}_3)$ . Another nitride of the metal  $(\text{Ti}_3\text{N}_4)$ , also formerly mistaken for metallic titanium, though containing 28 per cent. of nitrogen, is procured in copper-coloured scales by igniting the ammoniated titanic chloride  $(4\text{H}_3\text{N}, \text{TiCl}_4)$  in closed vessels, in a current of ammonia.\* If a current of dry

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\* Ammoniated columbic chloride yields a similar nitride when treated in like manner: the same remark applies also to the corresponding molybdic compound.

ammoniacal gas be transmitted over powdered titanic anhydride, heated to redness in a porcelain tube, a violet-coloured titanium dinitride ( $\text{TiN}_2$ ) is formed. So strong, indeed, is the attraction of titanium for nitrogen at a high temperature, that if a mixture of titanic anhydride and charcoal, both in a minute state of division, be heated to whiteness, and submitted to a current of nitrogen, the whole of the nitrogen is absorbed rapidly, while carbonic oxide escapes, and copper-coloured crystals, having the same composition as those obtained from the blast-furnace, are formed (Deville and Wöhler).

Pure titanium may be obtained by decomposing potassic fluotitanate ( $2\text{KF}, \text{TiF}_3$ ) with potassium, in a tube filled with pure hydrogen, and through which a current of pure hydrogen is maintained. It then forms a grey, amorphous powder, which burns in air with scintillation, and deflagrates in oxygen with dazzling brilliancy. Chlorine at ordinary temperature does not kindle titanium; but if heated in chlorine the metal burns with almost as much splendour as in oxygen. Titanium may also be obtained in prismatic crystals by heating sodium in the vapour of titanic chloride. It is soluble in hydrochloric acid with evolution of hydrogen, forming a colourless solution, from which ammonia precipitates a black hydrated protoxide.

(822) Three OXIDES OF TITANIUM probably exist—the protoxide, the sesquioxide, and the dioxide, or titanic anhydride.

The *protoxide* ( $\text{TiO} = 66$ ) has not been obtained in a pure state. It appears to be formed when titanic anhydride is heated in a crucible lined with charcoal; but where the anhydride is actually in contact with the charcoal, a film of metallic titanium, mixed with a portion of nitride, is obtained. The protoxide is a black powder nearly insoluble in acids, and is gradually oxidized by exposure to a high temperature in air, or by fusion with nitre.

If a solution of titanic acid in hydrochloric acid be digested with zinc, a purple, hydrated *sesquioxide* ( $\text{Ti}_2\text{O}_3, x \text{H}_2\text{O}$ ), or titanous titanate ( $\text{TiO}, \text{TiO}_2$ ) is deposited, which absorbs oxygen from the air with great rapidity, becoming white from the formation of titanic acid. Hydrochloric acid dissolves it sparingly, and forms a blue solution.

*Titanic anhydride*, or *Titanic dioxide* ( $\text{TiO}_2 = 82$ ).—This compound occurs in *menaccanite* and *iserine* as ferrous titanate; but more commonly it is met with in the uncombined condition, constituting the principal ore of the metal. It is found native under three distinct crystalline forms, each of which has a different specific gravity. Of these, the densest and most abundant is *rutile* (sp. gr. 4.25), it occurs in long striated prisms or needles of a brown colour, isomorphous with those of tin-stone. The second variety, *brookite* (sp. gr. 4.13), is found in right rhombic prisms, sometimes opaque, at others transparent, and of a pale brown; whilst the third variety, *anatase* (sp. gr. 3.9), is found in Dauphiny, in acute octohedra which are semi-transparent, and of a yellowish-brown or blue colour. Corresponding differences are observed in the titanic dioxide artificially prepared in the labora-



tory. Ebelmen obtained needle-shaped transparent yellow crystals of rutile of sp. gr. 4.283 by prolonged heating in a porcelain kiln, of a mixture of 1 part of powdered titanic dioxide and 5 parts microcosmic salt. Like stannic oxide, it may, when hydrated, be obtained in two isomeric forms possessed of different properties. In fact, the existence of two dissimilar modifications is a very usual occurrence in the case of metallic oxides possessed of feeble acid powers.

Pure titanic dioxide may be obtained by reducing rutile, or titanic iron-sand to a fine powder, and fusing it with thrice its weight of potassic carbonate. On treating the mass with hot water, an impure hydropotassic titanate remains. It is dissolved in hydrochloric acid, next mixed with an excess of ammonia, and the precipitate is digested in ammoniacal hydrosulphide, by which the tin, iron, and manganese are converted into sulphides, whilst the titanic acid remains unchanged: a solution of sulphurous acid then dissolves the sulphides, and a pure white hydrated titanic acid is left. The water may be expelled by heat, and by long-continued ignition the colour of the compound deepens, its specific gravity increasing till it acquires a density equal to that of rutile. In this state it is insoluble either in solutions of the alkalies, or in acids, except hydrofluoric acid and boiling oil of vitriol.

This anhydride may, however, be brought into solution by heating it with a fixed alkaline carbonate, and dissolving the residue with cold hydrochloric acid; the titanic acid may be precipitated by means of ammoniacal sesquicarbonate: it then forms a white gelatinous hydrate, which dries into a semi-transparent mass capable of reddening litmus. The liquid long remains turbid; it cannot be rendered clear by filtration, unless an excess of some ammoniacal salt be present. Hydrated titanic acid is insoluble in solutions of the caustic alkalies, but it yields definite salts with them. When fused with caustic potash it forms a transparent yellowish glass. The hydrated titanic acid is soluble in diluted hydrochloric acid; it is also dissolved by sulphuric acid, and forms a definite sulphate ( $\text{TiO}_2, \text{SO}_3$ ), which may be evaporated to dryness at a low temperature without undergoing decomposition. Both these acid solutions when diluted are decomposed by prolonged boiling, and the insoluble variety of titanic acid is precipitated. When the soluble hydrate is heated, it loses water and becomes converted into the anhydride. This compound becomes yellow on ignition, but recovers its whiteness on cooling. When fused with hydropotassic sulphate, titanic anhydride is dissolved, and may be obtained in solution by adding

water; it may thus be distinguished and separated from silica, which is not rendered soluble by this means.

(823) *Titanic sulphide* ( $\text{TiS}_2$ ) may be obtained in green scales; it is not soluble in the sulphides of the alkali-metals.

*Titanic chloride*, or *Tetrachloride of titanium*,  $\text{TiCl}_4 = 192$ ; *Rel. wt.* 96; *Sp. Gr. of vapour*, 6.836; *of liquid*, 1.761 at  $0^\circ \text{C}$ .; *Mol. Vol.*  $\square$ ; *Boiling-pt.*  $275^\circ$  ( $135^\circ \text{C}$ ).—This is a fuming volatile liquid, resembling stannic chloride. It may be obtained by decomposing pure titanic anhydride, intimately mixed with charcoal, and heated to redness in a porcelain tube, by means of a current of dry chlorine gas. It is a colourless liquid, which combines with a small quantity of water to form a crystallizable compound. A large quantity of water occasions its decomposition, hydrated titanic acid being separated. Deville obtained square prisms of metallic titanium by decomposing the vapour of the tetrachloride with sodium.

(824) CHARACTERS OF THE COMPOUNDS OF TITANIUM.—1.—The *titanous salts* are but little known; with the *carbonates of the alkali-metals* they give a blue precipitate, which becomes first brown and ultimately green.

2.—The *titanates* of the alkali-metals are of a yellowish-white colour: the normal salts are insoluble in cold water; hot water removes the alkali, while most of the titanic acid remains undissolved. Cold hydrochloric acid dissolves them, forming a solution which, when boiled, becomes turbid from deposition of titanic acid: *ammonia*, when added to this solution, produces a white precipitate. *Ammonic phosphate* gives a gelatinous precipitate when added to a hydrochloric solution of titanic acid. *Infusion of galls* produces an orange-coloured precipitate in the acid solution of the titanates; a precipitate of similar colour is produced by *potassic ferrocyanide*. In the reducing flame of the *blowpipe* the titanates give with microcosmic salt a beautiful purple or bluish glass, which becomes colourless in the oxidizing flame. This reaction distinguishes the titanates from the tantalates.

(825) *Estimation of Titanium*.—Titanium is always estimated in the form of titanic anhydride. Its solution in cold hydrochloric acid is not precipitated by sulphuretted hydrogen, a circumstance which may be taken advantage of in separating it from tin and cadmium, both of which are thrown down from the acid as insoluble sulphides. The solution is next mixed with tartaric acid, and supersaturated with ammonic hydro-sulphide: iron, nickel, cobalt, manganese, and zinc are thus separated in the form of sulphides. The solution is afterwards evaporated to dryness, and the tartaric acid is burned off; titanic anhydride is left, mixed with the salts of the earths and alkalies contained in the mixture; the residue is fused with caustic potash, redissolved in the cold with hydrochloric acid, and on boiling the liquid, to which a little diluted sulphuric acid has been added, the titanic acid is precipitated, collected, and converted into the anhydrous dioxide by ignition. This process, however, does not yield very accurate results; indeed the exact determination of the quantity of titanium in its compounds is a matter of considerable difficulty.

## § III. ZIRCONIUM AND THORIUM.

(825a) ZIRCONIUM ( $Zr^{iv} = 89.5$ ) is the elementary base of an oxide contained in the *zircon* and the *hyacinth*, which are zirconic silicates of similar composition ( $ZrO_2, SiO_2$ ). The metal is procured by heating the potassic fluozirconate ( $2KF, ZrF_4$ ) with potassium, and treating the residue when cold with diluted hydrochloric acid, by which everything except the zirconium is dissolved: it is thus left in a pulverulent form, and must be washed, first with a solution of ammoniac chloride, and then with alcohol; if water be used for the washing, the finely divided zirconium passes through the filter in suspension in the water. As thus obtained it is in the form of a black amorphous powder, which does not conduct a feeble voltaic current: under the burnisher it assumes a slightly metallic lustre: when heated in the air or in oxygen, it takes fire below redness and burns brilliantly, forming zirconia of snowy whiteness: diluted sulphuric and hydrochloric acids do not act on it. Hydrofluoric acid dissolves it with extrication of hydrogen, forming a fluoride closely resembling fluotitanic acid; it yields a number of fluozirconates with the fluorides of the basylous metals, which have the general formula  $2MF, ZrF_4$ . Boiling water gradually oxidizes amorphous zirconium; if heated with sulphur *in vacuo* it forms a brown pulverulent *disulphide*, which is not decomposed by sulphuric or hydrochloric acid, and is but slowly attacked by aqua regia. According to Troost (*Comptes Rendus*, lxi. 109) zirconium may also be obtained in crystalline plates of sp. gr. 4.15; it is less fusible than silicon. In this form it may be heated in air without taking fire, but burns in the oxyhydrogen flame. Caustic potash when melted with it oxidizes the crystals with evolution of hydrogen. Melted nitre and potassic chlorate do not act upon it. Concentrated nitric and sulphuric acid act on zirconium very slowly, and only when heated with it; hot hydrochloric acid also attacks it very slowly. Aqua regia when heated acts rapidly on it; but hydrofluoric acid whether strong or dilute dissolves it rapidly, even in the cold. Troost obtained this crystallized zirconium by heating 1 part of potassic fluozirconate ( $2KF, ZrF_4$ ) with  $1\frac{1}{2}$  aluminium in a crucible of gas coke heated to the fusing-point of iron: plates of zirconium are formed sometimes a centimetre broad, and may be freed from aluminium by digestion in hydrochloric acid diluted with twice its bulk of water. The zirconium is mixed with plates of an alloy of aluminium with zirconium, the proportions of which are variable. Zirconium is intermediate in properties between silicon and titanium, to which latter body it is more allied than to any other element, as is particularly seen in the properties of the zirconic tetrafluoride, and of the fluozirconates.

(825b) ZIRCONIA ( $ZrO_2 = 121.5$ ); Sp. Gr. 4.3.—Zirconium forms but one oxide, which Berzelius regarded as the sesquioxide, though most chemists now adopt the view of Dumas and of De Marignac, who consider it to be a dioxide, like silica. It may be obtained by fusing very finely powdered zircon with potassic or sodic hydrate, and saturating with hydrochloric acid. The excess of acid and moisture is expelled by evaporating nearly to dryness; on the addition of water, the zirconic chloride is dissolved, leaving the silica; the solution is decomposed by excess of ammonia: hydrated zirconia is thus precipitated and is washed and ignited. Upon applying heat, it glows brilliantly just before ignition, and becomes much denser. Zirconia forms a white infusible powder, which, after ignition, is insoluble in acids, with the exception of strong sulphuric acid. The hydrate is a gelatinous, bulky, white precipitate, very sparingly soluble in ammoniac sesquicarbonate. It is insoluble in the caustic alkalies. If the salts of zirconium be precipitated by an alkaline carbonate, the precipitate becomes redissolved if agitated with excess of the carbonate; a bicarbonate takes up still more, and by boiling the solution, a portion of zirconia is deposited. Zirconia when

fused with the carbonates of the alkali-metals decomposes them,  $\text{CO}_2$  being evolved, and a compound of zirconia with the alkali is formed. If a neutral solution of zirconic sulphate to which potassic sulphate has been added be boiled, a characteristic decomposition occurs, and a basic sulphate of zirconium falls, whilst hydropotassic sulphate is formed and remains dissolved. *Zirconic chloride* ( $\text{ZrCl}_4 = 186.8$ ; *Mol. Vol.*  $\square$ ; *Rel. wt.* 115.7; *Sp. Gr. of vapour*, 8.15) crystallizes in needles: it is soluble in water and in alcohol; the crystals effloresce in the air, and lose water and hydrochloric acid, leaving an oxychloride, which is soluble.

Zirconia is distinguished from alumina and glucina by its insolubility in the *caustic alkalies*. Its salts have a purely astringent taste; when their neutral solutions are boiled with one of *potassic sulphate*, a sparingly soluble subsulphate of the earth is formed. *Tincture of galls* gives a yellow precipitate in their solutions; *potassic ferrocyanide* does not produce a precipitate with them.

(826) THORINUM ( $\text{Th} = 238.0$ ) was discovered in 1829, by Berzelius, in a rare black mineral termed *thorite*, found in a syenitic rock in Norway. This metal, like aluminum, is procured from its chloride, which is a volatile compound obtained by heating an intimate mixture of thorina and finely divided charcoal in a current of dry chlorine. Thorinum much resembles zirconium, but takes fire considerably below redness, and burns with great brilliancy; the resulting oxide shows no traces of fusion. *Thorina* is probably a dioxide, and is remarkable for its high specific gravity (9.402). It is insoluble in solutions of the caustic alkalies, but is dissolved without difficulty in those of their carbonates. After it has been ignited it is no longer soluble in any acid except the concentrated sulphuric. Its salts have an astringent taste, and their solutions give a white precipitate with potassic ferrocyanide. Thorinic sulphate forms with potassic sulphate thorino-potassic sulphate ( $2\text{K}_2\text{SO}_4, \text{Th}_2\text{SO}_4, \text{H}_2\text{O}$ ), which is soluble in water, but is precipitated by a saturated solution of potassic sulphate. Thorinic sulphate exhibits the characteristic peculiarity of being precipitated by boiling its solution, but it is redissolved slowly on cooling: its crystals, like those of yttric sulphate, when heated become milk white without altering in form: oxalic acid gives, with salts of thorinum, even in acid solutions, a white insoluble oxalate of the metal.

§ IV. MOLYBDENUM: ( $\text{Mo} = 96$ ). *Sp. Gr.* from 8.615 to 8.636; *Dyad, Tetrad, and Hexad, as in*  $\text{Mo}''\text{Cl}_2$ ;  $\text{Mo}^{\text{iv}}\text{Cl}_4$ ;  $\text{Mo}^{\text{vi}}\text{O}_3$ .

(827) THE principal ore of molybdenum is the disulphide, a mineral which occurs chiefly in Bohemia and in Sweden, in appearance much resembling plumbago, and hence its name, from  $\mu\omicron\lambda\acute{\upsilon}\beta\delta\alpha\upsilon\alpha$ , 'a mass of lead.' Molybdenum is also occasionally found oxidized, in combination with lead, as plumbic molybdate. The metal may be obtained by roasting the pure native sulphide in a free current of air; the sulphur passes off as sulphurous anhydride, whilst the molybdenum also combines with oxygen, and remains behind in the form of molybdic anhydride. If this be mixed into a paste with oil and charcoal, and exposed to the heat of a smith's forge, in a crucible lined with charcoal, it is reduced to the metallic state. In this form molybdenum is white, brittle, and very difficult of fusion. The anhydride may also be reduced by heating it to redness in a porcelain tube in a current

of hydrogen : when the pulverulent metal is heated in the open air it is gradually oxidized, and finally converted into molybdic anhydride. It is readily oxidized by nitric acid ; if the metal be in excess, a soluble nitrate of the dioxide is obtained ; if the acid predominate, the oxidation proceeds further, and molybdic acid is formed : aqua regia produces similar results. Molybdenum is also oxidized when fused with nitre, and potassic molybdate is produced.

(828) OXIDES OF MOLYBDENUM.—Molybdenum forms three oxides ; the protoxide ( $\text{MoO} ?$ ), and the dioxide ( $\text{MoO}_2$ ) are both possessed of basic characters : the third ( $\text{MoO}_3$ ) reacts energetically upon bases, and yields well characterized salts.

The *protoxide* ( $\text{MoO} = 112 ?$ ) is precipitated from the solution of a molybdate in hydrochloric acid which has been reduced by means of a bar of zinc, on adding ammonia in excess ; it is thus thrown down as a black hydrate which absorbs oxygen from the air : it is soluble in a solution of ammoniac sesquicarbonate, but not in those of the fixed alkalies or their carbonates. It may also be obtained in the anhydrous form, by digesting molybdic anhydride with zinc and hydrochloric acid. According to Rammelsberg this oxide is a sesquioxide, and he doubts the existence of a protoxide.

The *dioxide* ( $\text{MoO}_2 = 128$ ) may be prepared by igniting a mixture of 2 parts of sodic molybdate and 1 part of sal ammoniac, and digesting the mass in a solution of potash, to remove any undecomposed molybdic acid. The residue, when well washed, is the pure anhydrous oxide, which has been reduced from molybdic acid by the hydrogen of the ammonia. It is of a dark brown colour, but it becomes purple if exposed to solar light ; it is nearly insoluble in acids. The hydrated dioxide may be obtained by digesting molybdic anhydride mixed with copper filings, in hydrochloric acid ; an excess of ammonia precipitates the dioxide of a rusty-brown colour, whilst the copper is retained in solution. Hydrated molybdic dioxide is soluble in pure water, but is precipitated by the addition of any salt. The solution gelatinizes on keeping. The salts which this oxide forms with acids are of a reddish-brown colour, or, if anhydrous, are nearly black.

If a solution of molybdic tetrachloride ( $\text{MoCl}_4$ ) be added, drop by drop, to a concentrated solution of the acid-molybdate of ammonium, a deep blue precipitate of molybdic tetramolybdate ( $\text{MoO}_3 \cdot 4\text{MoO}_3$ ) is formed. This compound is soluble in water, but is precipitated by the addition of any saline body. The addition of a small quantity of a stannous salt to a soluble molybdate reduces the molybdic acid, and produces this beautiful blue compound, which may serve as a test of the presence of molybdic acid : care must be taken not to add the tin salt in excess. The molybdic dimolybdate ( $\text{MoO}_3 \cdot 2\text{MoO}_3$ ) has a green colour.

(829) *Molybdic trioxide*, or *Molybdic anhydride* ( $\text{MoO}_3 = 144$ ) ; *Sp. Gr.* 3.49 ; *Comp. in 100 parts*, Mo, 66.6 ; O, 33.4.—This compound is obtained in the form of an impure trioxide by roasting the native molybdic disulphide at a low red heat : it remains behind as a dirty yellow powder ; caustic ammonia dissolves the trioxide, leaving ferric oxide and other impurities. The ammoniacal solution crystallizes on evaporation, and by a low red heat the ammonia is expelled, leaving the trioxide behind, of a pale

buff colour. The trioxide reddens moistened litmus-paper, and is sparingly soluble in water, forming a yellow solution. At a red heat it fuses to a straw-coloured glass of sp. gr. 3.49: it undergoes volatilization in open vessels, and is deposited on cool surfaces in brilliant transparent needles. No definite hydrated molybdic acid is known. When precipitated from its salts by the addition of an acid, it may be redissolved, if the acid be added in excess: with concentrated sulphuric acid it forms a yellow solution. It is also freely soluble in a solution of cream of tartar.

Molybdic acid forms well characterized salts, both normal and acid. Those of the alkalis are soluble. Normal or *diammonic molybdate* crystallizes in colourless square prisms. An *acid ammonic molybdate*  $[(H_4N)_4H_6MoO_4]$ , crystallizes readily in six-sided prisms. Various anhydro-molybdates of the alkalis have been formed, which contain as many as 3, 4, and even 5 atoms of the anhydride to 1 of fixed base. According to Delafontaine the soluble acid molybdates have a general formula,  $3M'_2O, 7MoO_3$ . Plumbic molybdate ( $PbMoO_4$ ) occurs native in crystals of a yellow colour; it is soluble in nitric acid, and in solution of caustic potash if the alkali be in large excess.

A solution of ammonic molybdate may be advantageously employed in certain cases to detect the presence of very small quantities of phosphoric acid in solution. The solution suspected to contain the phosphate must be acidulated with nitric acid, and the molybdate then added. The liquid becomes yellow, and on boiling, deposits a yellow crystalline precipitate, consisting of molybdic and phosphoric acids in combination with ammonia. According to Sonnenschein it contains 6.747 per cent. of ammonia, and about 3 per cent. of  $P_2O_5$ . Arsenic acid forms a similar compound with ammonic molybdate when the solutions are boiled.

Sonnenschein takes advantage of the insolubility of the phosphoric compound to detect small quantities of ammonia by its means. In order to prepare the test solution, he first procures the yellow precipitate, by adding ammonic molybdate to an acidulated solution of hydrodisodic phosphate, ignites the precipitate to expel the ammonia, adds nitric acid to the residue, in order completely to reoxidize any reduced molybdic acid, evaporates to dryness, and expels the nitric acid by ignition. A solution of sodic carbonate is employed to dissolve the remaining mixture of phosphoric and molybdic acids, and the solution is supersaturated with hydrochloric acid. This liquid, it is stated, will easily detect the presence of 1 part of sal ammoniac in 10,000 of water. Sodic salts are not affected by it, but strong solutions of the potassic salts yield a similar yellow precipitate.

(830) **SULPHIDES OF MOLYBDENUM.**—Three sulphides of molybdenum are known,  $\text{MoS}_2$ ,  $\text{MoS}_3$ , and  $\text{MoS}_4$ : the last two are sulphur-anhydrides.

*Molybdic disulphide*, or *Bisulphide of molybdenum* ( $\text{MoS}_2 = 160$ ; *Sp. Gr.* 4.6); *Comp. in 100 parts*, Mo, 60; S, 40.—This sulphide is the principal ore of the metal: it is a soft solid of a leaden-grey colour and metallic lustre. The disulphide may also be formed artificially by heating molybdic anhydride in the vapour of sulphur. It is unchanged by heat in closed vessels, but if roasted in the open air, sulphurous anhydride is formed and is volatilized, while molybdic anhydride remains. Nitric acid decomposes it, and converts the metal into molybdic acid; oil of vitriol also decomposes it when boiled upon it, forming a blue solution, whilst sulphurous anhydride escapes.

The *trisulphide* ( $\text{MoS}_3 = 192$ ) is precipitated by transmitting sulphuretted hydrogen through a solution of a molybdate, and adding hydrochloric acid. It is of a dark-brown colour, and forms sulphur salts with the sulphides of the alkali-metals. The potassium salt crystallizes in magnificent iridescent crystals ( $\text{K}_2\text{MoS}_3$ ). The *molybdic tetrasulphide* also combines readily with the sulphides of the alkali-metals.

A *molybdous chloride* ( $\text{MoCl}_2 = 167$ ) is obtained by dissolving the protoxide in hydrochloric acid. *Molybdic tetrachloride* ( $\text{MoCl}_4$ ) is procured by heating the metal in a current of dry chlorine: it forms a red vapour, which sublimes in deliquescent fusible crystals, in appearance resembling those of iodine. It may also be obtained in solution by dissolving the dioxide in hydrochloric acid.

A *chloromolybdic acid* sublimes in yellowish scales when the dioxide is heated in a current of chlorine. It is soluble both in water and in alcohol, and consists of  $(\text{MoCl}_4, 2\text{MoO}_3)$ , or  $(\text{MoO}_3\text{Cl}_2)$ . Compounds somewhat similar may be formed with many acidifiable metals, such, for example, as tungsten, chromium, and vanadium.

### (831) CHARACTERS OF THE SALTS OF MOLYBDENUM:—

1.—Little is known of the *molybdous salts*, or salts corresponding to the protoxide. They yield a dark-brown precipitate with the *hydrates of the alkalies* and their *carbonates*; the precipitate is soluble in excess of ammoniac sesquicarbonate, and is deposited again on boiling the liquid; *sulphuretted hydrogen* slowly produces a brown precipitate of hydrated sulphide, which is soluble in ammoniac hydrosulphide.

2.—The salts corresponding to the *dioxide* have a dark colour, and a metallic astringent taste. *Infusion of galls* produces with them a brownish-yellow solution; *potassic ferrocyanide* gives a dark-brown precipitate; *ammonia* a rusty-brown precipitate of the hydrated dioxide.

3.—The *molybdates* yield characteristic reactions with zinc, tin, and copper. With *zinc* in dilute acid solutions, the liquid becomes first blue, then green, and finally black, after which the addition of ammonia produces a deposit of hydrated molybdous oxide. The addition of a small quantity of *stannous chloride* in solution to a liquid containing a molybdate, produces the beautiful

blue molybdic tetramolybdate ( $\text{MoO}_3, 4\text{MoO}_3$ ), but care must be taken not to have the tin salt in excess, or the precipitate becomes of a dull green. *Copper filings* in similar solutions reduce the molybdic acid to the dioxide, which is precipitated as a brown hydrate by ammonia. *Before the blowpipe*, the compounds of molybdenum yield, in the oxidating flame, a colourless bead with borax, and with microcosmic salt; in the reducing flame they give a brownish-red bead with borax, and a green one with microcosmic salt.

Molybdenum is usually estimated in the form of the disulphide, of which 100 parts contain 60 of the metal.

§ V. TUNGSTEN: (Wolframium)  $\text{W} = 184$ ; *Sp. Gr.* 17.6;  
*Tetrad and Hexad, as in  $\text{WCl}_4$  and  $\text{WCl}_6$ .*

(832) TUNGSTEN is a metal found in small quantities in the mineral known as *Scheelite* or calcic tungstate ( $\text{CaWO}_4$ ), or else in *wolfram*, as a ferroso-manganous tungstate ( $\text{MnWO}_4, 3\text{FeWO}_4$ ). It is easily obtained from the calcic tungstate by digesting the powdered mineral in hydrochloric acid, which combines with and dissolves the calcium, but leaves the insoluble tungstic acid behind: from this compound the metal itself is procured, by heating it to bright redness in a current of hydrogen gas. It is thus left of a dark-grey colour, but it assumes a metallic lustre under the burnisher. If tungstic anhydride be made into a paste with oil, and heated intensely in a crucible lined with charcoal, for some hours, tungsten is obtained as a heavy iron-grey metal, which is very hard, and difficult of fusion. It may be heated in the air whilst in the compact state without sensible change, but in the pulverulent form it burns easily into tungstic anhydride. Aqua regia and nitric acid convert it into tungstic acid, and the same change is produced by heating it in contact with the alkalis or with nitre. Pulverulent tungsten is also oxidized and dissolved by boiling it in a solution of the caustic alkalis or of their carbonates. When tungsten is alloyed in the proportion of 9 or 10 parts with 90 of steel, it yields a metallic mass of extraordinary hardness.

(833) OXIDES OF TUNGSTEN.—Two of these are known, viz., a dioxide,  $\text{WO}_2$ , which does not form salts with acids, and an acid trioxide,  $\text{WO}_3$ . Wöhler attributes to an intermediate blue oxide the composition ( $\text{WO}_2, \text{WO}_3$ ).

The *dioxide* ( $\text{WO}_2$ ) is obtained as a brown powder by heating tungstic trioxide to low redness in a stream of hydrogen; or in copper-coloured scales, by adding tungstic anhydride to dilute hydrochloric acid in which some pieces of



zinc have been placed. In the latter form it attracts oxygen rapidly from the air, and is dissolved by a solution of caustic potash, with evolution of hydrogen and formation of potassic tungstate. Wöhler obtains the dioxide from wolfram by fusing; 1 part of this mineral with 2 parts of potassic carbonate: the melted mass is treated with boiling water, filtered, and mixed with a solution of  $1\frac{1}{2}$  part of ammoniac chloride. The solution is then evaporated to dryness, and the residue ignited; upon treating the mass with boiling water, the dioxide remains as a heavy black powder, which must be washed, first with a weak solution of potash, and afterwards with water. In this operation the hydrogen of the ammoniacal salt partially reduces the tungstic acid of the mineral.

With soda, tungstic oxide forms a remarkable compound of a yellow colour and metallic lustre, containing, according to Wright ( $\text{Na}_2\text{O}, \text{WO}_3, 2\text{WO}_3$ ). It crystallizes in cubes, and is not acted upon by any acid, or mixture of acids, except the hydrofluoric; the solutions of the caustic alkalies are equally without effect upon it: if heated in the air it is decomposed and partially converted into sodic tungstate. It is best obtained by fusing tin with an excess of the acid sodic tungstate: in order to remove the undecomposed sodic tungstate and free tungstic acid, the residue is treated in succession with concentrated solution of potash, water, and hydrochloric acid; finally it is washed with water. Corresponding compounds with potassium and lithium have also been obtained.

*Tungstic anhydride*, or *trioxide*, ( $\text{WO}_3=232$ ); often called *tungstic acid*; *Sp. Gr.* 6.12; *Comp. in 100 parts*, W, 79.32; O, 20.68.—Laurent considered that there were not fewer than six modifications of this acid, each of which formed a distinct class of salts; but the subsequent researches of Riche (*Ann. de Chimie*, III. l. 5), confirmed by those of Scheibler, appear to have shown that there are but two modifications in addition to the anhydride. These two different acids he terms the *tungstic* ( $\text{H}_2\text{WO}_4$ ), and the *metatungstic* acid ( $\text{H}_2\text{W}_4\text{O}_{13}$ ). De Marignac continues to apply the designation of *paratungstates* to a class of salts of the form of ( $5\text{M}_2\text{O}, 12\text{WO}_3, 2n + 1\text{H}_2\text{O}$ ), or ( $\text{M}_5\text{H}_3\text{W}_3\text{O}_7, n\text{H}_2\text{O}$ ), though he has not isolated any specific modification of acid from them.

*Tungstic anhydride* may be obtained from calcic tungstate by the process already described, or by decomposing wolfram with aqua regia, evaporating to dryness, and dissolving the liberated tungstic acid in ammonia; the ammoniac tungstate is purified by crystallization, and when heated in open vessels loses ammonia and water, and is converted into pure tungstic trioxide. This compound is a straw-yellow, tasteless, insoluble powder, which assumes a deeper orange tint when heated, the colour fading again as the temperature falls. In this form it is insoluble in acids, but is readily soluble in alkaline solutions; and when heated with solutions of the alkaline carbonates, it decomposes them with effervescence.

*Tungstic acid* ( $\text{H}_2\text{WO}_4$ ) is obtained in the form of a yellow powder by adding hydrochloric acid in excess to a boiling solution of the trioxide in any of the alkalies. The modification of acid

thus obtained forms two classes of salts, one of which is normal, the other acid in composition. Even the normal salts all redden litmus faintly.\* When mixed in the cold with an excess of hydrochloric acid, they are decomposed, and a white sparingly soluble hydrate of tungstic acid ( $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ ) is deposited.

The following table contains the formulæ of a few of the tungstates, and shows their complex character:—

Normal tungstates ...	$\text{M}_2\text{O} \cdot \text{WO}_3$	or $\text{M}_2\text{WO}_4$
Paratungstates ...	$5\text{M}_2\text{O} \cdot 12\text{WO}_3 \cdot 2n + 1\text{H}_2\text{O}$	$\text{M}_4\text{H}_3\text{W}_3\text{O}_{15} \cdot n\text{H}_2\text{O}$
Metatungstates ...	$\text{M}_2\text{O} \cdot 4\text{WO}_3 \cdot n\text{H}_2\text{O}$	$\text{M}_2\text{W}_4\text{O}_{13} \cdot n\text{H}_2\text{O}$
Potassic tungstate ...	$\text{K}_2\text{O} \cdot \text{WO}_3 \cdot 2\text{H}_2\text{O}$	$\text{K}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$
Sodic "	$\text{Na}_2\text{O} \cdot \text{WO}_3 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$
Potassic paratungstate ...	$5\text{K}_2\text{O} \cdot 12\text{WO}_3 \cdot 11\text{H}_2\text{O}$	$\text{K}_4\text{H}_3\text{W}_3\text{O}_{15} \cdot 5\text{H}_2\text{O}$
Sodic "	$5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 27\text{H}_2\text{O}^\dagger$	$\text{Na}_4\text{H}_3\text{W}_3\text{O}_{15} \cdot 13\text{H}_2\text{O}$
Ammonic "	$5(\text{H}_4\text{N})_2\text{O} \cdot 12\text{WO}_3 \cdot 11\text{H}_2\text{O}$	$(\text{H}_4\text{N})_4\text{H}_3\text{W}_3\text{O}_{15} \cdot 5\text{H}_2\text{O}$
Ditto (crystallized hot) ...	$5(\text{H}_4\text{N})_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$	$(\text{H}_4\text{N})_4\text{H}_3\text{W}_3\text{O}_{15} \cdot 2\text{H}_2\text{O}$
Sodio-potassic paratungstate	$4\text{K}_2\text{O} \cdot \text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 15\text{H}_2\text{O}$	$\text{K}_4\text{NaH}_3\text{W}_3\text{O}_{15} \cdot 7\text{H}_2\text{O}$
Acid sodic tungstate ...	$3\text{Na}_2\text{O} \cdot 7\text{WO}_3 \cdot 16\text{H}_2\text{O}$	$\text{Na}_4\text{H}_7\text{W}_4\text{O}_{12} \cdot 12\text{H}_2\text{O}$
Potassic metatungstate ...	$\text{K}_2\text{O} \cdot 4\text{WO}_3 \cdot 5\text{H}_2\text{O}$	$\text{K}_2\text{W}_4\text{O}_{15} \cdot 5\text{H}_2\text{O}$
Ammonic metatungstate	$3(\text{H}_4\text{N})_2\text{O} \cdot 8\text{WO}_3 \cdot \text{N}_2\text{O}_5$	$(\text{H}_4\text{N})_4\text{W}_4\text{O}_{15} \cdot \text{H}_4\text{NNO}_3$
and nitrate ...	$4\text{H}_2\text{O}$	$2\text{H}_2\text{O}$

*Potassic tungstate* is obtained by heating a strong solution of potassic carbonate to nearly its boiling-point and adding tungstic anhydride so long as it produces an effervescence: long slender, anhydrous, deliquescent needles of the tungstate are deposited from the solution as it cools; if redissolved, and allowed to recrystallize by spontaneous evaporation over oil of vitriol, at a temperature not exceeding  $50^\circ$  ( $10^\circ$  C.), large limpid prisms ( $\text{K}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) are formed; this salt is soluble in about half its weight of cold water. When pure it is not de-

\* Scheibler (*Journ. für Prakt. Chemie*, lxxxiii. 273) attributes to the tungstates formulæ much more complicated than those given by Riche; and De Marignac (*Ann. de Chimie*, III. lxi. 5) gives others for certain compounds yet more complicated than those of Scheibler, though the analyses of De Marignac agree almost exactly with Scheibler's.

The complexity of these formulæ has led Persoz to attempt to simplify them by altering the number assumed as the atomic weight of tungsten (*Ann. de Chimie*, IV. i. 93). He calls the atomic weight of tungsten, 153.3, and if we take for this new weight the symbol  $\text{Tu}$ , the formula for the anhydride will be  $\text{Tu}_2\text{O}_5$ . But if Regnault's determination of the specific heat of tungsten be correct, it is not probable that this number represents that of the atomic weight; and indeed the formulæ which Persoz proposes, when reduced, as needful, for the larger atomic weight of oxygen, are not less complicated than those for which he attempts to substitute them. I have, with one or two exceptions, adopted the formulæ of De Marignac as being the most symmetrical, and therefore the most probable, whilst they correspond quite as closely with the experimental results as any.

The researches of Graham (*Proceed. Roy. Soc.* xiii. 335), on the soluble colloids of the tungstic, molybdic, and other metallic acids, throw some further light upon their anomalies.

† De Marignac adopts the formula with  $28\text{H}_2\text{O}$ .

composed by the addition of a solution of the hydro-sodic carbonate, but if silica be present, a precipitate is occasioned by this test. *Acid-tungstate of potassium* may be obtained as  $(K_2W_2O_7)$  by fusing an equivalent of the foregoing salt with one of the tungstic anhydride, or by adding a second equivalent of tungstic anhydride to a hot solution of an equivalent of the normal salt, when it crystallizes in hydrated plates with  $H_2O$ . A sparingly soluble *paratungstate*  $(K_2H_3W_2O_{11} \cdot 5H_2O)$  is obtained by transmitting a current of carbonic anhydride through a solution of the normal tungstate: it is deposited in pearly scales. The normal *sodic tungstate*  $(Na_2WO_4 \cdot 2H_2O)$  crystallizes readily in thin pearly rhomboidal plates. The *paratungstate* of De Marignac  $(Na_2H_3W_2O_{11} \cdot 13H_2O)$  may also be obtained crystallized in large efflorescent oblique prisms. This salt becomes modified by long boiling of its solution, which then on evaporation deposits long 8-sided prisms of an acid salt  $(Na_2H_7WO_4 \cdot 17H_2O)$ . Another acid salt containing only 12 instead of 17  $H_2O$ , is also known, and if either of these salts be fused at a full red heat, an insoluble salt  $(Na_2O \cdot 4WO_3)$  is left on treating the mass with water. No normal ammoniac tungstate is known, but the *paratungstate* is easily obtained by digesting the anhydride in excess of ammonia: it is a sparingly soluble salt which at ordinary temperatures crystallizes in two distinct forms, either in delicate needles, or in thin brilliant plates, both having the same composition  $[(H_4N)_2H_3W_2O_{11} \cdot 5H_2O]$ . If crystallized at a little below the boiling-point, it is deposited in hard brilliant rhomboidal needles which contain 2 instead of 5  $H_2O$ . A *tungstous tungstate*  $(WO_3 \cdot WO_3)$ , of a splendid blue colour, somewhat analogous to the molybdic molybdates, may be obtained by a partial reduction of tungstic acid, either by hydrogen gas, or by strongly igniting ammoniac tungstate in closed vessels, or by digesting tungstic anhydride with zinc and hydrochloric or sulphuric acid.

The most important native ore of tungsten is *wolfram*, which occurs in hard prismatic crystals of a dark brown colour; it is regarded as a mixture, in variable proportions, of ferrous and manganous tungstates. Its specific gravity is very high, being about 7.3. It was this circumstance that gave rise to the name *tung-sten*, the term being a combination of two Swedish words, implying 'heavy stone.' This mineral is decomposed when boiled with hydrochloric acid, or with aqua regia, the tungstic acid remaining undissolved. It is also readily decomposed by fusion with nitre or with sodic carbonate, and a soluble tungstate of the alkali-metal is formed.

*Metatungstic Acid*  $(H_2W_4O_{13}$  or  $H_2O \cdot W_4O_{12})$ .—The salts of this acid colour litmus of a wine-red, and crystallize generally with facility. They pass readily when in solution into the salts of tungstic acid: the change is gradual in neutral solutions at ordinary temperatures, more rapid in boiling liquids, or on the addition of a powerful acid, and the conversion is instantaneous if the hot liquid is mixed with a caustic alkali or alkaline carbonate in excess. The metatungstates are always prepared by the action of hydrated tungstic acid upon the tungstates.

If the white hydrated acid  $(H_4WO_7 \cdot H_2O)$ , obtained by the action of hydrochloric acid in the cold upon the soluble tungstates, be neutralized by bases, it furnishes salts which are identical with the ordinary tungstates; but if one of

the soluble normal tungstates, such as potassic tungstate, be boiled with the white hydrate of the acid in the proportion of an atom of each until the solution no longer becomes turbid on the addition of an acid, a new salt, *potassic metatungstate* ( $K_2W_4O_{12}, 8H_2O$ ) is formed, and is deposited in square based octohedra: a second salt containing only  $5H_2O$  crystallizes in delicate needles, after adding alcohol to a strong solution of the first salt. A sodic metatungstate with  $10H_2O$  crystallized in brilliant octohedra may be obtained by operating as for the first potash salt. Ammonic metatungstate  $[(H_4N)_2W_4O_{12}, 8H_2O]$  crystallizes in brilliant fusible octohedra. The metatungstates, when mixed with nitric acid, do not at once yield a precipitate of the metallic acid.

*Baric metatungstate* ( $BaW_4O_{12}, 9H_2O$ ) may be obtained in crystals with a fatty lustre, by mixing a warm concentrated solution of ammonic metatungstate with an equivalent quantity of one of baric chloride; and by decomposing baric metatungstate with its exact equivalent of diluted sulphuric acid, a solution of the metatungstic acid is obtained.

De Marignac has found that when acid potassic tungstate is boiled with gelatinous silica, the liquid becomes alkaline, silica is dissolved, and a new salt, a *silico-tungstate*, is formed. The acid is unstable, but it may be obtained crystallized at ordinary temperatures in square tables ( $4H_2O, SiO_2, 12WO_3, 20H_2O$ ); or in cubo-octohedra, which contain  $18H_2O$ , by evaporation at a rather high temperature. Two other silicated tungstic acids appear to exist: each of the three forms is soluble in alcohol; with the alkali-metals they form very soluble salts.

(834) SULPHIDES OF TUNGSTEN.—There are two sulphides of this metal, the disulphide and the trisulphide.

The *disulphide* ( $WS_2$ , *Sp. Gr.* 6.26) was obtained by Riche in a pure form by heating, in a covered clay crucible, an intimate mixture of equal parts of acid potassic tungstate and sulphur. After fusion at a very high temperature for half an hour, the mass is poured out, powdered, and washed with boiling water. The disulphide is left in the form of bluish-black slender crystals, which feel unctuous to the touch, and stain paper or the skin like plumbago; it admits of being consolidated by pressure, and might, probably, be used in the manufacture of drawing-pencils.

The *trisulphide* ( $WS_3$ ) may be obtained by dissolving tungstic anhydride in a solution of dipotassic sulphide, and precipitating by the addition of an acid: it is slightly soluble in pure water.

The trisulphide is a strong sulphur acid; with dipotassic sulphide it forms an orange-yellow crystallizable compound. These sulpho-salts may be formed by heating the tungstates of the alkali-metals with an excess of sulphur.

PHOSPHIDES OF TUNGSTEN.—Phosphorus enters into combination with tungsten, when its vapour is passed over the metal in a finely-divided state, and heated to redness in a glass tube; a dull, dark grey powder ( $W_3P_4$ ), difficult of oxidation, is thus formed. Another compound ( $W_5P$ ) is formed in beautiful crystalline groups like geodes, by reducing a mixture of 2 atoms of phosphoric and 1 atom of tungstic anhydride, at a very high temperature, in a crucible lined with charcoal: brilliant six-sided steel-grey prisms, of *sp. gr.* 5.207, are thus obtained. It is a good conductor of electricity. It is oxidized with difficulty when heated, and is not attacked by acids.

Both the CHLORIDES of this metal, the tetrachloride  $WCl_4$ , and the hexachloride  $WCl_6$ , are volatile: they are decomposed by water into hydrochloric acid and the corresponding oxide of tungsten. The *hexachloride* (*Sp. Gr. of Vapour*, 11.86; Debray) is formed by passing pure and dry chlorine over heated metallic tungsten; it fuses at  $361^{\circ}.4$  ( $183^{\circ}$  C.), and is of a bronze colour, but by exposure to the air quickly acquires a violet hue, owing to its partial decomposition by the absorption of moisture.

The *diorydichloride* ( $\text{WO}_2\text{Cl}_2$ ) may be obtained in yellow volatile crystalline scales, by passing dry chlorine, over either the tungstous oxide or tungstic anhydride when heated to redness. It is sometimes termed chlorotungstic acid. The red volatile compound, formerly supposed to be a perchloride, is, according to Riche, an oxytetrachloride of the form ( $\text{WOCl}_4$ ; *Sp. Gr. of Vapour*, 10.74, Debray).

Tungstic tetrachloride ( $\text{WCl}_4$ ) absorbs ammonia, and by a gentle heat, the whole of the chlorine is expelled in the form of sal ammoniac, leaving a black powder consisting of  $2\text{WN}_3$ ,  $\text{WH}_4\text{N}_3$ . When this powder is heated in the air it burns, evolving ammonia and leaving a residue of tungstic anhydride (Wöhler): it is not soluble in acids.

(835) CHARACTERS OF THE SALTS OF TUNGSTEN.—The compounds of this metal are not poisonous. No salts corresponding to tungstic dioxide are known.

The *tungstates* in solution are colourless. They are not precipitated either by *sulphuretted hydrogen* or by *ammonic hydro-sulphide*. A *bar of tin*, placed in their acidulated solution in a vessel from which air is excluded, produces a deep violet-coloured liquid, owing to the reduction of the acid to a lower degree of oxidation. Zinc, stannous chloride, and other reducing agents, in the presence of acids, produce a like result. The addition of any stronger acid to a boiling solution of the tungstates causes the separation of a yellow precipitate of tungstic acid which is soluble in phosphoric and in tartaric acid. They yield *before the blowpipe*, with borax, a colourless transparent glass, which becomes yellow in the reducing flame, and blood-red on cooling. With microcosmic salt (621) they give a beautiful blue in the reducing flame, which becomes yellow or colourless in the oxidating flame; the addition of a little metallic tin to the bead favours the production of the blue colour.

Tungsten is always estimated in the form of tungstic anhydride, 100 grains of which contain 79.32 of the metal.

## § VI. COLUMBIUM—TANTALUM.

(835a) COLUMBIUM, or NIOBIUM ( $\text{Nb} = 94$ ) was discovered in the year 1801 by Hatchett, who found it in a black mineral from Massachusetts, termed *columbite*. In the following year Ekeberg obtained a new metal, which he termed *Tantalum* ( $\text{Ta} = 182$ ), from the *tantalite* and *ytthro-tantalite* of Sweden.

These two metals were asserted by Wollaston to be identical—an opinion generally received until Rose showed that the American mineral contained a metallic acid different from that furnished by the tantalite: this acid he termed the *niobic*; and its metallic constituent, *niobium*, is the columbium of Hatchett. Rose at the same time stated that associated with this was a second metallic acid, which he termed the *pelopic*, but this he subsequently ascertained to be a compound of the metal which he called niobium.

A volatile *chloride* of this metal ( $\text{NbCl}_3$ ); *Sp. Gr. of Vapour*, 9.6; *Fusing-pt.*  $381^\circ.2$  ( $194^\circ \text{C.}$ ); *Boiling-pt.*  $464^\circ$  ( $240^\circ.5 \text{C.}$ ) may be obtained; as well as

a volatile *fluoride* of similar constitution, which furnishes crystallizable double fluorides that have been studied by De Marignac. It also yields an oxychloride  $\text{NbOCl}_3$ , and an oxyfluoride  $\text{NbOF}_3$ .

Niobium and tantalum are too rare to need a detailed description here: they have a certain analogy with silicon,—tantalic anhydride was believed by Rose to be a dioxide  $\text{Ta}_2\text{O}_5$ ; but the subsequent researches of De Marignac, and the crystalline form of potassio-tantalic fluoride ( $2\text{KF}, \text{TaF}_6$ ) seem to show that it is rather to be regarded as  $\text{Ta}_2\text{O}_5$ .

These two metals belong rather to the group of phosphorus than to that of silicon, and the same remark applies to vanadium.

Hermann supposed the ytthro-tantalite of Siberia to contain a new metal, analogous to columbium, to which he gave the name of *Ilmenium*; but he has since proved the so-called ilmenic acid to be a mixture of the tantalic and niobic anhydrides.

## § VII. VANADIUM ( $V=51.3$ .)

(836) VANADIUM is one of those rare metals at present known only as chemical curiosities: it was discovered in 1830, by Sefström, in a Swedish iron ore from Taberg, which yielded bar iron remarkable for its malleability; but its most abundant ore is vanadinite [ $3(\text{Pb}_2\text{VO}_3)\text{PbCl}_2$ ], a mineral isomorphous with pyromorphite [ $3(\text{Pb}_2\text{PO}_4)\text{PbCl}_2$ ]; vanadinite has been found at Zimapan in Mexico, at Wanlockhead in Scotland, and more recently in Chili; lately Wöhler has found vanadium accompanying some of the ores of uranium and iron. Quite recently a more abundant supply of this metal has been met with by Roscoe in the cupriferous stratum of the new red sandstone at Alderley Edge in Cheshire, and we are indebted to the last-named chemist for a new investigation of the principal compounds of vanadium.

Berzelius believed that he had isolated the metal by heating vanadic anhydride in a covered porcelain crucible with potassium, but the brilliant metallic-looking powder, according to Roscoe, still retains oxygen. Several anomalies have been cleared up by this discovery, as vanadium will now take its place in the series of phosphorus, with which it forms isomorphous compounds, instead of being, as was supposed, allied to molybdenum and tungsten. The metal itself appears not to have been isolated hitherto.

(837) OXIDES OF VANADIUM.—At present 4 oxides of the metal are known, but it is not improbable that a fifth  $\text{V}_2\text{O}$  may be hereafter discovered, completing the series  $\text{V}_2\text{O}$ ,  $\text{V}_2\text{O}_2$ ,  $\text{V}_2\text{O}_3$ , and  $\text{V}_2\text{O}_5$ . The oxide  $\text{V}_2\text{O}_2$ , according to Roscoe, is the body regarded by Berzelius as the metal;  $\text{V}_2\text{O}_3$  was his vanadous oxide  $\text{VO}$ ,  $\text{V}_2\text{O}_4$  was his vanadic oxide  $\text{VO}_2$ , and the anhydride  $\text{V}_2\text{O}_5$ , his vanadic acid  $\text{VO}_3$ .

*Salts of the oxide  $\text{V}_2\text{O}_3$*  (the *vanadyl* of Roscoe), are lavender coloured in solution. Roscoe obtains them by reducing a dilute solution of the anhydride in sulphuric acid, by means of zinc, of cadmium, or of sodium amalgam. The solution absorbs oxygen from the air with great avidity, and owing to its de-oxidizing power it bleaches indigo and litmus as quickly as chlorine itself, but the colour returns on exposure to the air. The oxide has been obtained as a bright grey metallic-looking powder by transmitting a current of dry hydrogen charged with the vapours of the oxychloride  $\text{VOCl}_3$ , through a tube containing ignited charcoal. It is soluble in dilute acids with evolution of hydrogen.

The *sesquioxide*, *Sp. Gr.* 4.72 ( $\text{V}_2\text{O}_5 = 150.6$ ), is obtained from vanadic anhydride, by reducing it, by means of a stream of hydrogen, or by charcoal: it is a black, crystalline, brittle mass, resembling graphite in appearance, and, like it, conducts electricity. Roscoe states that the presence of a minute quantity of phosphoric acid prevents the complete reduction of the anhydride by hydrogen, to this condition. In this form it does not combine either with acids or with

bases. If heated in air for some time it absorbs oxygen, forming the *divanadium-tetroxide* ( $V_2O_4 = 166.4$ ), as a black anhydrous powder, and even at common temperatures this absorption of oxygen goes on until the mass becomes converted into blue crystals of the same oxide.

Salts corresponding to the sesquioxide  $V_2O_3$  of a brown or green colour, according as they are neutral or acid, may be obtained by reducing the sulphate of vanadic anhydride by means of magnesium, which only carries the reduction to this stage.

The oxide  $V_2O_3$  forms salts with acids; they have a blue colour, and when mixed with the hydrates of the alkalies furnish a grey hydrate of this oxide; in this form it rapidly absorbs oxygen, and becomes first brown and then green. This oxide appears also to possess feebly acid properties, for it combines with bases.

Solutions of divanadium tetroxide may be obtained by reducing the solution of sulphate of vanadic acid by sulphuretted hydrogen or sulphurous acid, when a bright blue liquid is obtained.

*Vanadic anhydride* ( $V_2O_5 = 182.6$ ; *sp. gr.* 3.49) is of a brownish-red colour; at a red heat it fuses without further change, and crystallizes in rhombic prisms on cooling, becoming incandescent from evolution of latent heat in the act of passing from the vitreous into the crystalline condition. It is sparingly soluble in water, to which it communicates a yellow tint: the solution is powerfully acid and reddens litmus strongly. It forms both normal and acid salts: the normal salts when first prepared are yellow, but in a few hours they spontaneously become white. The most important of these salts is the *ammonic vanadate*  $(H_4N)VO_3$ , the *metavanadate* of Roscoe, from which the acid itself is usually obtained. Ammonic vanadate is procured by putting pieces of sal ammoniac into a crude solution of potassic vanadate (such as is prepared by the deflagration of the slag obtained from the iron ore of Taberg, with nitre, after the excess of alkali has been neutralized with hydrochloric acid): the ammonic vanadate being insoluble in a saturated solution of ammonic chloride is gradually deposited in small crystalline grains. Cold water dissolves it sparingly, but it is much more soluble in hot water: when heated in the open air the ammonia is expelled, and pure vanadic anhydride is left. The *acid ammonic vanadate*,  $2(H_4NVO_3), V_2O_5$ , yields crystals of an orange colour. If mixed with tincture of galls, these salts give a deep black liquid, which preserves its blackness even when much diluted: it forms a very permanent writing ink, since it is not destroyed either by acids, which turn it blue, or by alkalies, or by chlorine.

Vanadic anhydride appears to combine in different proportions with the inferior oxides of the metal, forming compounds which are either of a green or a purple colour. It also combines with many acids in definite proportions, such as the compound  $(V_2O_5, 3SO_3)$ . Several of these compounds crystallize with facility.

**VANADIUM CHLORIDES.**—The pure chlorides of vanadium have not yet been examined. According to Roscoe several oxychlorides exist, viz.,  $V_2O_5Cl$ ,  $VOCl$ ,  $VOCl_2$ , and  $VOCl_3$ . The most important is the liquid last-mentioned, which was formerly regarded as the trichloride.

*Vanadic oxytrichloride*,  $VOCl_3$ ; *Sp. Gr. of Vapour* 6.108; *of liquid* 1.841 at  $14^\circ.5$  C.; *Boiling-pt.*  $260^\circ$  ( $126^\circ.7$ ); *Rel. wt.* 86.8; *Mol. Vol.*  $\square$ ; *Mol. wt.* 173.8.—This is a yellow fuming volatile liquid analogous to phosphoryl chloride  $POCl_3$ . It is immediately decomposed by water into vanadic and hydrochloric acids;  $VOCl_3 + 3H_2O = H_2VO_4 + 3HCl$ . This oxychloride may be obtained by heating a mixture of vanadic anhydride and charcoal in a current of hydrogen, after which it is heated in a current of dry chlorine; or it may be procured at once by passing dry chlorine over the sesquioxide,  $3V_2O_5 + 6Cl_2 = V_2O_4 + 4VOCl_3$ . This oxychloride remains liquid at  $-5^\circ$  ( $-15^\circ$  C.).

Vanadic oxytrichloride is decomposed if heated with hydrogen, lower solid oxychlorides being formed.

*Vanadium Nitrides.*—Two of these are known, VN, and VN<sub>2</sub>. The *dinitride*, VN<sub>2</sub>, is obtained as a black powder by passing ammoniacal gas over the oxytrichloride, heating to expel sal ammoniac, washing with solution of ammonia, and drying over sulphuric acid. The other nitride, VN, may be obtained by igniting the foregoing compound intensely in a current of dry ammonia—as steel white brittle compound.

(838) CHARACTERS OF THE COMPOUNDS OF VANADIUM.—1. The salts corresponding to the *divanadium tetroxide* V<sub>2</sub>O<sub>4</sub> yield blue solutions, which give a deep blue black colour with *tincture of galls*, and a grey precipitate with the hydrated *alkalies*, soluble in excess of the precipitant; the precipitate becomes red by exposure to the air. *Potassic ferrocyanide* gives a yellow precipitate, which becomes greenish when exposed to the air. The *sulphides* of the alkali-metals give a brownish-black precipitate, readily soluble in excess, and forming a magnificent purple liquid.

2.—The *vanadates* are usually red or yellow: they have a powerfully astringent taste: when treated either with sulphuretted hydrogen, or sulphurous acid, or when boiled with sulphuric acid and either alcohol or sugar, they give a beautiful blue solution, a reaction that distinguishes them from the chromates, which under these circumstances furnish a green liquid. *Before the blowpipe* with borax in the reducing flame, compounds containing vanadium give a green glass, which becomes yellow in the oxidating flame.

§ VIII. ARSENICUM: (As'''=75). *Theoretic Sp. Gr. of vapour*, 10.167; *Observed*, 10.6; *of solid, from 5.70 to 5.959*; *Atomic Vol.*  $\frac{1}{2}$  or  $\square$ ; *Rel. wt.* 150; *Molecular Vol.* As<sub>2</sub>  $\square$ ; \* *Triad, as in AsCl<sub>3</sub>*; *rarely Pentad, as in As(CH<sub>3</sub>)<sub>4</sub>I.*

(839) ARSENICUM, or *arsenic*, in various states of combination, was known to mankind before the Christian era. This element presents many analogies with phosphorus, and with nitrogen: it is considered by several French writers to belong to the non-metallic elements. It, however, conducts electricity with facility, and possesses a high metallic lustre. Arsenicum generally presents itself in the form of an alloy with some other metal, especially with iron, or with cobalt, nickel, copper, or tin. It is found occasionally in the native state, and it sometimes occurs united with oxygen and certain metals, constituting arseniates, such as those of iron, copper, and lead. More rarely it occurs united with sulphur, either as the red sulphide (As<sub>2</sub>S<sub>3</sub>), realgar, or as the yellow sesquisulphide, As<sub>2</sub>S<sub>3</sub>, known as orpiment.

The greater part of the arsenic of commerce is prepared from mispickel (FeAsS), an arsenical sulphide of iron furnished abundantly by the Silesian mines; and from the arsenides of nickel and cobalt, which yield arsenious sesquioxide as a secondary pro-

\* Four atoms of arsenicum enter into the formation of one molecule of its vapour; in this respect this element corresponds with phosphorus.



duct in the ordinary process of working these ores. The separation of the arsenic is effected by roasting the mineral in a manner similar to that employed for driving off sulphur; but the arsenious sesquioxide which is produced, being less volatile, more valuable, and more deleterious, is condensed in large chambers, through which the flues from the furnaces pass. The emptying of these chambers, which is performed about once in six weeks, is an operation attended with danger to the workmen, from the poisonous and irritating nature of the finely-powdered arsenious sesquioxide. In order in some degree to protect the men whilst thus engaged, they are cased in leather, with glazed apertures for the eyes, and are made to cover their mouths and nostrils with damp cloths, which arrest most of the acrid particles. Much of the sesquioxide obtained from these chambers is in the form of a fine powder; it is still very impure, and it is therefore again sublimed in iron pots, the upper part of which is kept moderately cool; here it is condensed into a transparent, half-fused, vitreous mass. The lower portions only of this sublimate are pure, and these are sold as white arsenic; the upper are either resublimed, or are employed for the purpose of furnishing arsenicum. In order to obtain the metal, the sublimed sesquioxide is powdered, mixed with charcoal, or with twice its weight of black flux, and heated in an earthen crucible, upon the top of which a second inverted crucible is luted, and screened from the fire by means of a perforated iron plate. The reduced metal is condensed in the upper crucible.

*Properties.*—Metallic arsenic, or *arsenicum*, has a brilliant, dark steel-grey lustre; it is very brittle, and is easily reduced to powder. When heated to  $356^{\circ}$  ( $180^{\circ}$  C.) in closed vessels, it begins to volatilize without fusing, and crystallizes indistinctly, as it is condensed, in rhombohedra, which are isomorphous with those of antimony. Its vapour is colourless, and possesses a powerful, oppressive, alliaceous odour. The metal may be exposed to a dry air without undergoing change: when exposed in a moist state to the air it is slowly oxidized, and a substance known as *fly-powder* is formed; it is probably a mixture of arsenious sesquioxide and arsenicum, though it is regarded by some chemists as a suboxide. If the metal be heated in open vessels it absorbs oxygen, burns with a lurid bluish flame, and is converted into arsenious anhydride, which is condensed as a white, mealy powder, upon cool bodies in the neighbourhood. When thrown in fine powder into chlorine gas it takes fire spontaneously, and is converted into arsenious chloride. Bromine, iodine, and sulphur

also combine readily with arsenicum when aided by a gentle heat. Nitric acid easily oxidizes the metal, and converts it into arsenic acid: if deflagrated with nitre, it is converted into potassic arseniate. Hydrochloric acid exerts but little action on the metal, but if the hydrochloric be mixed with nitric acid, or with potassic chlorate, the metal is rapidly converted into arsenic acid.

A small quantity of arsenic is added to lead to facilitate its assuming the globular form in the manufacture of shot. In the form of arsenious sesquioxide it is extensively used in the preparation of green and yellow pigments; it is likewise employed to prevent smut in grain, but the practice is to be reprobated; it is also used in the manufacture of flint glass as an oxidizing agent, for converting the ferrous oxide into ferric oxide, in order to get rid of the green tinge which ferrous oxide communicates to the vitreous mass. Its employment as a poison for vermin has often been made a pretext for procuring it for criminal purposes.

OXIDES OF ARSENIC.—These are two in number: the sesquioxide or arsenious anhydride,  $\text{As}_2\text{O}_3$ , and arsenic anhydride,  $\text{As}_2\text{O}_5$ ; both have acid properties, no basic oxide being known.

(840) *Arsenious acid, Arsenious sesquioxide, or Arsenious anhydride* ( $\text{As}_2\text{O}_3 = 198$ ); *Sp. Gr. of vapour*, 13.85; *Comp. in 100 parts*, As, 75.75; O, 24.25; *Mol. Vol.* ( $\text{As}_2\text{O}_3$ )<sub>2</sub> =  \*; *Rel. wt.* 198. —This compound is the *white arsenic* of the shops. It is prepared upon the large scale during the roasting of arsenical ores in the manner already described. It exists in two modifications, a vitreous and a crystalline form. When purified by resublimation and freshly obtained, it is in semi-transparent, vitreous, lamellated masses; but by exposure to the air, it gradually becomes opaque, and of a yellowish-white colour. This change advances slowly, from the exterior towards the interior, so that the mass is often opaque at the surface whilst it remains transparent in the centre. Both varieties of arsenious anhydride are freely soluble in hot hydrochloric acid; when this solution is boiled, a portion of the arsenic is volatilized in the form of trichloride; as the liquid cools the excess crystallizes in transparent anhydrous octohedra, consisting of uncombined arsenious sesquioxide; but when the transparent variety has been employed, the formation of each crystal is marked by the emission of a flash of light which is perceptible in a darkened room. The opaque variety exhibits no such phenomenon in crystallizing from its solution.

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\* The molecular volume of this body is anomalous, the density of its vapour being double of that which might from analogy have been expected.

A hot solution of ammonia also dissolves white arsenic freely, and deposits it in anhydrous octohedra of the uncombined sesquioxide on cooling, mixed with prismatic crystals of ammonic arsenite,  $\text{H}_4\text{N}, \text{AsO}_3$  (Bloxam; *Journ. Chem. Soc.* 1862, 297). Guibourt found the opaque variety to have a specific gravity of 3.699; it is less dense than the transparent form, the specific gravity of which he states to be 3.7385. The two varieties also differ in their solubility: according to Bussy, water dissolves nearly three times as much of the transparent as of the opaque form. A cold saturated solution of the vitreous variety gradually deposits its excess in the form of the opaque anhydride, and retains between 2 and 3 per cent. in solution; the liquid reddens litmus. Mere grinding to a fine powder converts the transparent into the opaque variety, and reduces its solubility. Heat, however, gradually reconverts the opaque into the vitreous modification, so that long-continued boiling renders the opaque as soluble as the vitreous form. It is therefore difficult to state the precise degree of solubility of either form of the compound, because the two varieties are liable to be formed in varying proportion in the course of an experiment. The largest proportion which water will dissolve at the boiling-point is between 11 and 12 per cent. Both nitric acid and aqua regia dissolve the sesquioxide, and convert it into arsenic acid.

Arsenious sesquioxide, when heated to about  $380^\circ$  ( $193^\circ.3$  C.), softens and is sublimed without fusing, being condensed in transparent octohedra upon warm surfaces, but it occasionally forms long prismatic needles, isomorphous with those of antimonious oxide ( $\text{Sb}_2\text{O}_3$ ). Its vapour is without odour; it is colourless, and contains 1 volume of vapour of arsenic and 3 volumes of oxygen, condensed into 1 volume.

*Arsenites.*—Arsenious acid is soluble in solutions of the alkalis and of their carbonates: with potassium and sodium it forms soluble compounds which do not crystallize. Its acid properties are feebly marked, but it appears to be tribasic, the most usual formula of its salts being  $\text{M}'_3\text{AsO}_3$  (Bloxam). A solution of *tripotassic* arsenite has been used medicinally for many years under the name of *Fowler's solution*. The arsenites of the metals of the earths (particularly tricalcic diarsenite) are nearly insoluble in water, but are readily dissolved by acids. *Hydrocupric* arsenite ( $\text{CuHAsO}_3$ ) is, in a commercial point of view, the most important of these salts; it is of a delicate and beautiful green colour, constituting the pigment sold under the name of *Scheele's green*. It is prepared by dissolving 1 part of arsenious anhydride and 3 parts of

potassic carbonate in 14 of water, and adding the liquid to a boiling solution of 3 parts of cupric sulphate in 40 of water; the shade of green may be varied by altering the proportion of arsenious anhydride. This compound is a dangerous poison. It is soluble in acids and in ammonia. When heated it is partially decomposed, and arsenious anhydride sublimes. The *Schweinfurt green*, which is also used largely as a pigment, is a cupric arsenite and acetate ( $3\text{CuAs}_2\text{O}_4 \cdot \text{Cu}_2\text{C}_2\text{H}_3\text{O}_2$ ), made by mixing equal parts of arsenious anhydride and cupric acetate, in solution at a boiling temperature, adding an equal bulk of cold water, and allowing the mixture to stand for some days. *Triargentic* arsenite ( $\text{Ag}_3\text{AsO}_3$ ) is of a canary-yellow colour; it is obtained by the addition of a solution of argentic nitrate to one of tripotassic arsenite. If a slip of bright copper foil be introduced into a solution of arsenious acid in hydrochloric acid, a grey film of reduced arsenicum is deposited on the copper; if zinc be substituted for copper, arseniuretted hydrogen is evolved (845, 846). Arsenious acid in solution may readily be converted into arsenic acid by acidulating the liquid with hydrochloric acid, warming it, and gradually adding potassic chlorate in small quantities. Arsenious acid is indeed a powerful reducing agent; its solution in hydrochloric acid reduces auric chloride; it bleaches potassic permanganate, and reduces potassic anhydro-chromate to a chromic sesquisalt.

If a solution of arsenious acid in sodic carbonate be mixed with a little starch, and a solution of iodine or of chlorine be added till the starch turns blue, the arsenious is converted into arsenic acid; this reaction forms the basis of a volumetric process for the determination of iodine and chlorine in solution.

If a minute fragment of arsenious sesquioxide be heated with a similar portion of sodic acetate in a small test-tube, the characteristic and peculiarly offensive odour of kakodyl is perceived.

(841) *Arsenic anhydride*, or *Arsenic acid* ( $\text{As}_2\text{O}_5 = 230$ ); *Comp.* in 100 parts, As, 65.22; O, 34.78.—This compound is obtained by treating arsenious sesquioxide with nitric acid in slight excess, and then boiling down to dryness in a platinum vessel. A white, somewhat deliquescent mass of arsenic anhydride remains: by slow evaporation of its solution arsenic acid may be obtained in hydrated crystals.

E. Kopp (*Ann. de Chimie*, III. xlviii. 106) found, when operating on a large scale, that if a concentrated solution of the acid was stirred briskly at a temperature not exceeding  $59^\circ$  ( $15^\circ$  C.), a semi-liquid mass was often obtained, filled with elongated prisms or rhomboidal plates ( $\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ ): they are extremely deliquescent; when heated to  $100^\circ$  C. they become liquid, lose water, and gradually deposit a white creamy mass, consisting of small needles, which, when dried by

pressure between folds of filtering-paper, were found to consist of ( $\text{As}_2\text{O}_3, 3\text{H}_2\text{O}$ , or  $\text{H}_3\text{AsO}_3$ ). In order to obtain the hydrate ( $\text{As}_2\text{O}_3, 2\text{H}_2\text{O}$ , or  $\text{H}_4\text{As}_2\text{O}_7$ ), Kopp evaporated at a temperature ranging between  $284^\circ$  and  $356^\circ$  ( $140^\circ$  and  $180^\circ \text{C.}$ ); if a very concentrated solution of this so-called hydrate be kept for some time at  $392^\circ$  ( $200^\circ \text{C.}$ ), and then be gradually raised to  $402^\circ.8$  ( $206^\circ \text{C.}$ ) the liquid suddenly boils up, becomes pasty, and is converted into a pearly mass of dazzling whiteness, consisting of ( $\text{As}_2\text{O}_3, \text{H}_2\text{O}$ , or  $\text{HAsO}_3$ ), which it is difficult to obtain free from the anhydride. At a temperature below redness it becomes anhydrous; all these different forms when dissolved in water, reproduce a liquid like the original solution. In preparing arsenic acid, Kopp employs 300 kilos. of nitric acid, sp. gr. 1.35, to 400 kilos. of arsenious sesquioxide, and by adding the nitric acid gradually, no application of artificial heat is necessary. No attempts to procure the dibasic and monobasic forms of arsenic acid have hitherto been successful; indeed I find that it forms but a single stable hydrate, the so-called *dihydrate* ( $\text{H}_4\text{As}_2\text{O}_7$ , or  $2\text{H}_2\text{O}, \text{As}_2\text{O}_3$ ), and this is obtained whether the solution be evaporated over sulphuric acid at the ordinary temperature, or in the open air at any temperature not exceeding  $302^\circ$  ( $150^\circ \text{C.}$ ): in this way hard brilliant prisms of the dihydrate are procured; at a temperature of  $500^\circ$  ( $260^\circ \text{C.}$ ) these become anhydrous, and finally, if the mass be suddenly heated to redness, it fuses, and becomes decomposed into arsenious sesquioxide and oxygen.

If a current of sulphurous acid be transmitted through a solution of arsenic acid it is slowly reduced to the state of arsenious acid, whilst sulphuric acid is formed,  $\text{H}_3\text{AsO}_4 + \text{H}_2\text{SO}_3$  becoming  $\text{H}_3\text{AsO}_3 + \text{H}_2\text{SO}_4$ . Arsenic acid has recently been employed in calico-printing to some extent as a substitute for tartaric and phosphoric acids, but its employment is dangerous if the waste products are allowed to run into the streams. Its chief consumption is in the preparation of magenta dye from aniline.

*Arseniates.*—The arsenic is a powerful tribasic acid, expelling the volatile acids from their combinations, and decomposing the carbonates with effervescence. The salts of this acid have the general formula  $\text{M}'_3\text{AsO}_4$ , and of the 3 atoms of its basic hydrogen, 1, 2, or 3, may consist of a metal. It forms a series of soluble crystallizable salts with the alkali-metals, which present considerable interest, as they are isomorphous with the tribasic phosphates. Hydrodisodic arseniate, the commercial *arseniate of soda*, is a manufactured product of considerable importance. It is best obtained by saturating arsenious anhydride with crude soda-ash, and deflagrating the dry residue in a reverberatory furnace with a suitable proportion of sodic nitrate. By adding caustic soda in excess to arsenic acid, an efflorescent salt ( $\text{Na}_3\text{AsO}_4, 12\text{H}_2\text{O}$ ) may be obtained on evaporation, crystallized in prismatic needles. If to a hot solution of arsenic acid, sodic carbonate be added till effervescence ceases, the salt which is obtained on evaporation ( $\text{Na}_2\text{HAsO}_4, 12\text{H}_2\text{O}$ ) corresponds in form and composition to the rhombic hydrodisodic phosphate, though more usually it crystallizes with  $7\text{H}_2\text{O}$ ; and by adding to a

solution of this compound a quantity of arsenic acid equal to that which it contains, a deliquescent salt ( $\text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$ ) is procured, which crystallizes with difficulty. The corresponding potassio-dihydric arseniate crystallizes in bold brilliant octohedral crystals ( $\text{KH}_2\text{AsO}_4$ ): it is readily prepared by deflagrating equal parts of arsenious anhydride and nitre, then dissolving the residue in water, and allowing it to crystallize. All these salts may be rendered anhydrous by heat, but when redissolved, they recover their basic water. An ammonio-magnesian arseniate ( $\text{H}_4\text{NMgAsO}_4 \cdot 6\text{H}_2\text{O}$ ) may be procured in the form of prismatic crystals isomorphous with those of the corresponding phosphate, by mixing a solution of magnesian sulphate containing an excess of ammonia with a neutral or ammoniacal solution of an arseniate of one of the alkali-metals: it is sometimes used as a precipitant for arsenic acid; it is very sparingly soluble in weak ammoniacal solutions; when dried at  $100^\circ \text{C}$ . 2 atoms of the salt lose 11  $\text{H}_2\text{O}$ , and the residue contains 60.52 parts of arsenic anhydride. A brick-red triargentic arseniate ( $\text{Ag}_3\text{AsO}_4$ ) is precipitated when any arseniate in solution is mixed with a solution of argentic nitrate: it is readily soluble in excess either of nitric acid or of ammonia, and is characteristic as a test of arsenic acid. Hydrocupric arseniate ( $\text{CuHAsO}_4$ ) is of a pale greenish-blue colour; the tricalcic and triplumbic diarsenates are white; whilst ferric and uranic salts give yellowish white arseniates: all these are readily soluble in excess of diluted nitric acid.

(842) **SULPHIDES OF ARSENIC.**—Arsenicum and sulphur may be melted together in all proportions; but they form several well-defined compounds: of these, the most important are realgar,  $\text{As}_2\text{S}_2$ ; the sesquisulphide, or orpiment,  $\text{As}_2\text{S}_3$ ; and the diarsenic pentasulphide,  $\text{As}_2\text{S}_5$ .

*Realgar* ( $\text{As}_2\text{S}_2 = 214$ ); *Sp. Gr.* 3.356.—This substance is occasionally found native in ruby-red prismatic crystals; it may be prepared artificially, by heating together 9 parts of arsenicum and 4 of sulphur, or 198 parts of arsenious anhydride with 112 of sulphur;  $2\text{As}_2\text{O}_3 + 7\text{S} = 2\text{As}_2\text{S}_2 + 3\text{SO}_2$ . When heated in closed vessels, realgar melts, and afterwards is sublimed without decomposition. The sublimed mass is hard, brittle, transparent, and of a beautiful red colour. Realgar is insoluble in water: it is readily attacked by nitric acid and by aqua regia, but not by hydrochloric acid; potassio disulphide dissolves it and forms a double sulphide. Caustic potash decomposes it, leaving a brown arsenical sub-sulphide ( $\text{As}_{12}\text{S}$ ) undissolved. Realgar is one of the ingredients of *white Indian fire*, which is often used as a signal light: it is composed of a mixture of 7 parts of sulphur, 2 of realgar, and 24 of nitre.

*Arsenious sesquisulphide*, or *Orpiment* ( $\text{As}_2\text{S}_3 = 246$ ); *Sp. Gr.* 3.48; *Comp. in 100 parts*, As, 60.98; S, 39.02.—Orpiment (*auri pigmentum*, so called from its golden-yellow colour) is occasionally

found native in crystals which have the same form as those of realgar—viz., the oblique rhombic prism: these crystals are flexible; they have a yellow colour and a brilliant lustre. It may be prepared artificially by transmitting a current of sulphuretted hydrogen through a solution of arsenious acid, or of any of the arsenites, in hydrochloric acid; it then falls as a brilliant yellow amorphous powder. If the solution be very dilute, part of the sesquisulphide is retained in solution, forming a yellow liquid; by exposure to the air the excess of sulphuretted hydrogen escapes, and the sesquisulphide is gradually and completely deposited.

Orpiment is insoluble in water and in dilute acids, but it is decomposed by nitric acid and by aqua regia. It fuses easily, and when heated in air burns with a pale blue flame. In closed vessels it may be sublimed without undergoing decomposition. Ammonia and the fixed alkalies dissolve it, and form colourless solutions containing an alkaline arsenite and sulpharsenite. The ammoniacal solution is sometimes used for dyeing yellow, since by exposure to air the ammonia evaporates, leaving the yellow sesquisulphide firmly adherent to the fibre. Orpiment is also soluble in solution of ammoniac sesquicarbonate. This sesquisulphide is a feeble sulphur-acid, so that ammoniac sulphide and the sulphides of the alkali-metals in solution dissolve it easily, and form double sulphides, which are decomposed on the addition of an acid. Orpiment is the colouring ingredient in the pigment called *King's yellow*, which is a mixture of arsenious sesquioxide with this sulphide.

*Diarsenic pentasulphide* ( $\text{As}_2\text{S}_5 = 310$ ; *Comp. in 100 parts*, As, 48.39; S, 51.61) corresponds in composition to arsenic anhydride. When a stream of sulphuretted hydrogen is transmitted through a solution of arsenic acid, a yellow precipitate, resembling orpiment in appearance, and consisting of a mixture of orpiment and sulphur, is very gradually separated (Rose). But by decomposing a dilute aqueous solution of the sulphosalt ( $\text{Na}_3\text{AsS}_4$ ), by the addition of an acid, a bright yellow precipitate of  $\text{As}_2\text{S}_5$  is obtained. Upon the application of heat, this sulphide fuses into a dark liquid, and forms a reddish-yellow glassy substance as it cools; it may be sublimed in closed vessels. It is soluble in the caustic alkalies, decomposes the carbonates with effervescence if boiled with their solutions, and forms crystallizable compounds with the sulphides of the metals of the alkalies and alkaline earths. The trisodic sulpharseniate may be procured by saturating a solution of 10 parts of soda (reckoned as  $\text{Na}_2\text{O}$ ) with sulphuretted hydrogen, adding an equal quantity of soda, and then dissolving 26 parts of orpiment and 7 of sulphur in the liquid by the aid of heat; on evaporation, the sodium-salt is obtained in pale yellow crystals. The sulphur-salt of potassium ( $2\text{K}_2\text{S}_2\text{As}_2\text{S}_5$ ) may be made by transmitting sulphuretted hydrogen through the solution of the hydridopotassic arseniate. When an aqueous solution of this sulphur-salt of arsenic is mixed with alcohol, it undergoes decomposition, and by evaporating the alcoholic solution, after separating the insoluble portion by fil-

tration, a still higher sulphide ( $\text{AsS}_3$ ) was obtained by Berzelius, in brilliant yellow crystalline scales.

(843) COMPOUNDS OF ARSENICUM WITH HYDROGEN.—Arsenic forms two combinations with hydrogen; one of these ( $\text{As}_4\text{H}_3$ ?) is solid at ordinary temperatures, and of a chestnut-brown colour; it is obtained by employing a plate of arsenicum as the platinode during the voltaic decomposition of acidulated water. The other is a gaseous body ( $\text{H}_3\text{As}$ ) of considerable importance; it corresponds in composition to the gaseous phosphuretted hydrogen.

*Trihydride of arsenic; Arseniuretted hydrogen* ( $\text{H}_3\text{As}=78$ ); *Rel. wt.* 39; *Theoretic Sp. Gr.* 2.645, *Observed*, 2.695; *Mol. vol.*  —This remarkable gaseous compound is an exceedingly poisonous body; it is colourless, and has a foetid alliaceous odour; it is sparingly soluble in water, and possesses neither acid nor alkaline qualities. It consists of half a volume of arsenical vapour and 3 volumes of hydrogen condensed into 2 volumes.

The composition of the gas may be thus represented—

			By weight.		By volume.		Sp. gr.
Arsenic	As	=	75 or 96.15		0.5 or 0.25	=	2.5417
Hydrogen	H <sub>3</sub>	=	3      3.85		3.0    1.5	=	0.1036
	<u>AsH<sub>3</sub></u>	=	<u>78    100.00</u>		<u>2      1.0</u>	=	<u>2.6453</u>

By a temperature of  $-40^\circ$  it is reducible to a limpid colourless liquid, which remains liquid at  $-166^\circ$  ( $-110^\circ \text{ C.}$ ). Arseniuretted hydrogen is inflammable, and burns with a bluish-white flame, which deposits arsenicum upon cold bodies introduced within it, and arsenious anhydride upon those held above. It is also decomposed when caused to pass through tubes heated to a temperature a little short of redness, arsenicum being deposited as a steel-grey crust, whilst hydrogen gas escapes: if a current of dry sulphuretted hydrogen be transmitted over the heated crust a yellow sublimate of orpiment is formed, which is not acted on by a current of dry hydrochloric acid gas. These reactions distinguish the arsenical from the antimonial crust, which by similar treatment gives a dark orange-coloured sulphide decomposable by a current of dry hydrochloric acid gas. Chlorine decomposes arseniuretted hydrogen with flame, forming hydrochloric acid, and causing the deposition of a solid brown arsenical hydride. Concentrated nitric acid also absorbs the gas completely, whilst arsenic acid is formed. The gas is entirely absorbed by a solution of cupric sulphate, sulphuric acid being liberated, whilst arsenide of copper is precipitated. Argentic nitrate is also decomposed by arseniuretted hydrogen, arsenic acid being formed while silver is precipitated;  $\text{AsH}_3 + 8\text{AgNO}_3 +$



$4\text{H}_2\text{O} = 8\text{HNO}_3 + \text{H}_3\text{AsO}_4 + 4\text{Ag}_2$ . In the application of Marsh's test (p. 668) the presence of a small quantity of nitric acid prevents the formation of gaseous hydride, and causes the deposition of the solid hydrate. Solution of corrosive sublimate likewise dissolves the gas completely, a compound of calomel and arsenide of mercury being formed. It is also largely absorbed by oil of turpentine, with which it forms a crystalline compound.

Pure arseniuretted hydrogen may be prepared by decomposing with sulphuric acid diluted with three parts of water, an arsenide of zinc, obtained by heating equal weights of powdered arsenicum and granulated zinc in an earthen retort; the fused mass is removed by breaking the retort, and is subsequently powdered. The greatest care is required not to inhale any portion of this deadly gas.

(844) ARSENIUS CHLORIDE, or *Trichloride of arsenic* ( $\text{AsCl}_3$ , = 181.5); *Rel. wt.* 90.75; *Sp. Gr. of vapour*, 6.3; *of liquid at 32° (0° C.)*, 2.205; *Boiling-pt.* 273°·2 (134° C.); *Mol. vol.*  .—Only one compound of arsenic with chlorine is known. It is produced either by the combustion of the metal in chlorine, or by distilling a mixture of 1 part of arsenicum and 6 parts of corrosive sublimate, or still more easily by heating arsenious anhydride in a current of dry chlorine gas: it condenses as a heavy, colourless, oily-looking liquid, which remains liquid at  $-20^\circ\cdot 2$  ( $-29^\circ \text{C.}$ ); it fumes when exposed to the air, and is immediately decomposed by water into arsenious and hydrochloric acids.

ARSENIUS IODIDE, or *Tri-iodide of arsenic* ( $\text{AsI}_3$ , = 456; *Sp. Gr. of vapour*, 16.1; *of solid*, 4.39; *Mol. Vol.*  ; *Rel. wt.* 228), may be prepared by subliming a mixture of 3 parts of iodine and 1 part of the metal in a flask; it forms brick-red brilliant flakes. It may also be obtained by digesting 3 parts of powdered arsenicum and 10 of iodine in 100 of water; on evaporation the clear liquid yields red hydrated crystals, which become anhydrous when heated to their fusing-point: it is soluble in alcohol.

A *tribromide* may be formed by analogous means; it is a crystalline solid at all temperatures below  $68^\circ$  ( $20^\circ \text{C.}$ ), of sp. gr. 3.66; it boils at  $428^\circ$  ( $220^\circ \text{C.}$ ).

The *trifluoride* may be prepared by distilling 5 parts of fluor-spar, mixed with 4 of arsenious anhydride and 10 of concentrated sulphuric acid. It is a fuming colourless liquid, which corrodes glass rapidly, and is decomposed by water.

(845) CHARACTERS OF THE COMPOUNDS OF ARSENIC.—Arsenicum forms, with most of the metals, alloys which are generally brittle and easily fusible. The compounds of this metal are all highly poisonous:\* the substance which has the best claim to be

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\* For a singular statement respecting the arsenic eaters of Styria, the reader is referred to a paper by Mr. Heisch, in the *Pharmaceutical Journal* for May, 1860, p. 556.

considered as an antidote to it, is the freshly-precipitated hydrated ferric oxide, which should be suspended in water, and given freely, as early as possible after the poison has been swallowed. It is only applicable when arsenic or arsenious acids have been taken uncombined with bases, as it forms an insoluble ferric arseniate; the arsenious acid being partially oxidized by the excess of hydrated sesquioxide, which is thereby reduced to the form of ferrous oxide. Calcined magnesia may be used if the ferric oxide be not at hand. In cases of arsenical poisoning, putrefaction of the body after death is retarded in a remarkable degree; indeed, in various instances where the body has been disinterred several months after death, it has been found to have been sufficiently preserved from decay, to allow many of the principal viscera to be distinguished. In these cases, it has not unfrequently happened that yellow patches of orpiment have been observed in various parts of the alimentary canal, although it has been ascertained that the poison had been swallowed in the form of white arsenic. These patches of orpiment are occasioned by the disengagement of sulphuretted hydrogen from the decomposition of the tissues, by which the arsenious sesquioxide becomes partially converted into the sesquisulphide.

Arsenic can be identified in quantities so minute, as to be inappreciable by the balance. In minerals which contain it, its presence is revealed by the peculiar garlic odour which it emits when a fragment is heated in the reducing flame with sodic carbonate on charcoal, *before the blowpipe*. When in solution, the compounds of arsenic may be detected by transmitting through the solution, acidulated with hydrochloric acid, a stream of *sulphuretted hydrogen* for six hours; a yellow precipitate is thus produced, which must be further examined as follows: the liquid must be exposed to a temperature of about  $104^{\circ}$  ( $40^{\circ}$  C.), in a shallow vessel for six hours, to allow the gas to escape, and the precipitate to subside completely; the clear liquid must be decanted, and the precipitate collected on a small filter. A few drops of ammonia will dissolve it, and on evaporating this solution in a watch-glass by means of a water-bath, the arsenious sesquisulphide will be left. This substance is then subjected to the process of *reduction*, by mixing it with three times its bulk of black flux,\* or with a mixture of 1 part of potassic cyanide and 3 parts of sodic carbonate, previously well dried, and introducing it into

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\* A mixture of potassic carbonate and charcoal obtained by deflagrating equal weights of cream of tartar and nitre in a red-hot earthen crucible.

a glass tube of the diameter of a common quill, care being taken not to soil the sides of the tube. The mixture is heated strongly by the blowpipe, and the arsenicum is condensed as a brilliant mirror-like ring of steel-grey lustre in the upper part of the tube. The reaction which occurs when black flux is used, may be represented as follows:  $2\text{As}_2\text{S}_3 + 6\text{K}_2\text{CO}_3 + 6\text{C} = \text{As}_4 + 6\text{K}_2\text{S} + 6\text{CO} + 6\text{CO}_2$ .

Cadmic sulphide gives a yellow precipitate with sulphuretted hydrogen, but it is insoluble in ammonia: stannic salts also give a yellow precipitate with sulphuretted hydrogen, but no metallic sublimate when they are submitted to the process of reduction.

In addition to the preceding tests, arsenious acid may be readily detected in a *neutral* solution, by the production of a yellow precipitate with *ammonia-nitrate of silver*. This reagent is prepared by adding ammonia to a solution of argentic nitrate in very slight excess, so as nearly, but not entirely, to redissolve the precipitate of argentic oxide which is at first formed: the clear liquid is decanted for use. The yellow precipitate is tri-argentic arsenite, which is freely soluble both in ammonia and in nitric acid. As, however, the tribasic phosphates give a yellow precipitate with ammonia-nitrate of silver, and this precipitate also is soluble both in nitric acid and ammonia, a second test should be tried—viz., the *ammonia-sulphate of copper*, which is prepared from a solution of cupric sulphate, by the addition of ammonia, with the same precautions as those prescribed for the preparation of the silver test. In neutral solutions containing an arsenite, this copper test occasions a green precipitate consisting of hydrocupric arsenite: it is soluble both in ammonia and in acids. The arsenites of silver and copper are formed immediately that the tests are added; the sulphide of arsenic does not appear at first if the metal be present as arsenic acid, as the compounds of arsenic acid are decomposed by hydrosulphuric acid more slowly than those of any other metal which is precipitable by this reagent.

(846) *Search for Arsenic in Organic Mixtures*.—In the greater number of cases, however, where the search for arsenic becomes important, it is mixed with articles of diet, with the contents of the stomach, or with other matters of organic origin, which render preliminary measures needful in order to get rid of them. If the substance be in the liquid form, any sediment which it may contain must be examined for solid particles of undissolved arsenious anhydride, which are frequently found, and to which the preceding tests are readily applied. If any solid particles of arsenious

anhydride be found, their reduction is easily effected by drawing off a tube to the thickness of a crowquill, sealing one end, dropping in the suspected fragment, adding a minute quantity of dried sodic carbonate, and then a few small fragments of charcoal; upon ignition, the metal is sublimed, and may be recognized by the steel-grey ring which it forms in the cool portion of the tube.

If no solid particles of the anhydride be visible, the liquid is boiled and filtered, and divided into three portions, one of which is set aside in case of accident.

A second portion is submitted to *Reinsch's test*; it is for this purpose acidulated with about  $\frac{1}{10}$  of its bulk of pure hydrochloric acid, and boiled with bright slips of pure electrotype copper foil for half an hour.\* If any arsenical compound be present, the metal will be reduced upon the surface of the copper foil. The copper is then withdrawn from the liquid, washed, dried at  $100^{\circ}$  C., and introduced into a narrow glass tube (of about the diameter of a quill), which is then drawn out to a capillary neck, taking care not to heat the copper foil in this operation. The tube is shown in fig. 357. The foil, and the portion of the tube which contains it, are then heated nearly to red-

FIG. 357.



ness; the arsenic combines with oxygen derived from the air in the tube, and it condenses in beautiful transparent octohedra of arsenious anhydride on the contracted cool part of the tube. The same experiment must be first tried with the copper and hydrochloric acid employed alone, in order to ascertain their purity before employing them as tests. The presence of nitrates or of chlorates interferes with the application of Reinsch's test, as the copper foil becomes dissolved when boiled with the acidulated solution under these circumstances. If, however, the liquid be first acidulated with an excess of hydrochloric acid, and be evaporated by a gentle heat on a water-bath, the residue may be subjected to Reinsch's process as usual. A slip of metallic copper occasions precipitates in many metallic solutions when acidulated with hydrochloric acid and boiled with them; such, for example, as antimony, bismuth, tin, silver, mer-

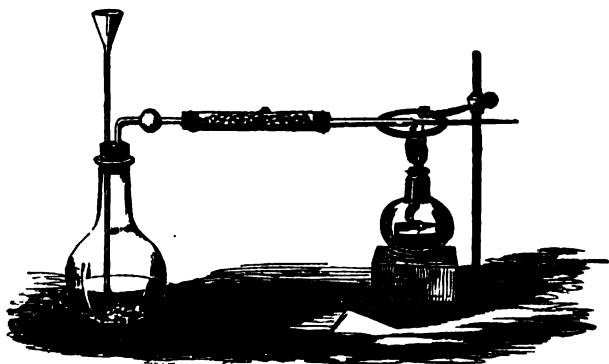
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\* Dilute solutions of arsenious acid in hydrochloric acid may be evaporated below  $100^{\circ}$  C. without loss of arsenious chloride, but if the mixture be distilled to dryness in a retort, the chloride passes over in the last portions, and may thus be separated from most other metals: the distillate may then be submitted to Reinsch's or Marsh's test. This furnishes an excellent method of procedure in many cases. See a paper by Dr. Taylor, in *Guy's Hosp. Reports*, vol. vi.

cury, lead, and cadmium: cadmium is not precipitable from a strongly acid solution. Of these precipitates mercury is the only one which, like arsenicum, is volatilized by heat in the metallic form, but the sublimate, when viewed with the microscope, is seen, if mercurial, to consist of globules, and is thus easily distinguished from arsenic. Moreover the arsenical crust by resublimation is converted into arsenious anhydride, whilst no such change takes place with mercury. Antimony becomes oxidized, and sublimes with difficulty in needles, not in octohedra, and may be identified in the manner described at p. 681.

The third portion of the liquid is subjected to *Marsh's test*: the application of this test depends upon the formation of arseniuretted hydrogen, and the subsequent deposition of arsenicum from it by suitable application of heat:—A wide-mouthed flask, fig. 358, of about 6 oz. (170 c. c.) capacity, is charged with a

FIG. 358.



little pure granulated zinc, or with fragments of magnesium; through the cork a tube funnel is passed to within an inch of the bottom; a bulb tube, bent to a right angle, passes just through the cork, the outer horizontal tube *c*, being loosely filled with calcic chloride to arrest any particles of fluid which might be carried up by the effervescence; it is prolonged by fitting into it with a cork, a piece of German tube, *a*, free from lead and drawn out to a capillary termination. Some distilled water is next introduced by the funnel, and a little pure sulphuric acid added to cause a steady evolution of hydrogen. When all the atmospheric air is expelled, the flame of a spirit-lamp is placed under the point where the capillary contraction commences: if after ten minutes, the temperature of the glass being at a red heat, no indications of any metallic deposit show themselves, the

materials used are sufficiently pure. Whilst the heat is still maintained, the suspected liquid is to be poured through the funnel into the bottle; if arsenic be present, immediate voltaic decomposition ensues, part of the arsenic combines with the nascent hydrogen; arseniuretted hydrogen is formed, and the gas is decomposed as it passes through the heated tube, the metal being deposited in the form of a steel-grey ring just beyond the spot where the heat is applied. If, instead of heating the capillary tube, the gas be kindled as it escapes, it will be found to burn with the peculiar flame of arsenic if the quantity be at all considerable, and if a piece of cold white porcelain, such as a crucible lid, be introduced into the burning jet, the more combustible hydrogen is burned, and brown or grey mirror-like spots of reduced arsenic may be obtained upon the cold plate.\* Tartar-emetic, if present, would, however, produce antimoniuiretted hydrogen, which, by its decomposition, would give rise to appearances in the tube and on the porcelain resembling those of arsenicum. Fleitmann has shown that if the hydrogen be generated by dropping zinc into a strong boiling solution of caustic potash or soda, and then adding the suspected arsenical liquid, the hydrogen which is given off contains the arsenic if this metal be present, but does not form antimoniuiretted hydrogen with an antimonial compound. The antimonial spots also immediately disappear when a drop of ammoniac sulphide, in which a little sulphur is dissolved, is added, and the solution, by its spontaneous evaporation, leaves the orange-coloured antimonious sesquisulphide; but the arsenical crusts are scarcely acted on by the ammoniac sulphide (Dr. Guy). The chief practical difficulty in the use of Marsh's test, arises from the inconvenient way in which liquids containing organic matter frequently froth up during the operation. The best method of preventing this consists in first heating the suspected liquid with about a tenth of its bulk of hydrochloric acid, and adding a small quantity of potassic chlorate: the organic matter is thus destroyed, and after the liquid has become cool, it may be safely added to the zinc and sulphuric acid in the apparatus.

The process by sulphuretted hydrogen and subsequent reduction is extremely delicate, and open to no objection except the length of time required. Marsh's test is one of extraordinary

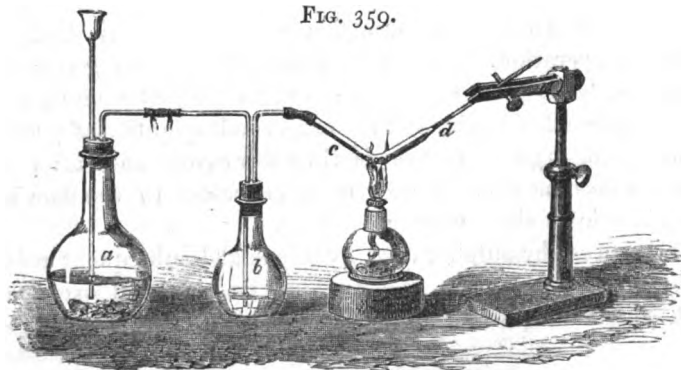
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\* According to Blondlot the presence of minute quantities of nitric acid prevents the formation of gaseous arseniuretted hydrogen and causes the deposition of the solid arsenide upon the zinc.

delicacy, and the results are easily and quickly attained: Reinsch's test is also easy of application, and is extremely delicate; but they all act very slowly when the arsenic is in the form of arsenic acid. The arsenical crusts deposited in the glass tube are readily sublimed by a gentle heat, and may be converted into arsenious anhydride, which forms brilliant minute octohedral crystals, and these again may be subjected to the test of the ammonia-nitrate of silver.

Although it may not be possible to detect arsenic in the fluids submitted to examination, it not unfrequently happens that the coats of the stomach, and sometimes the liver, will yet contain the poison in sufficient quantity to render its identification practicable. The best mode of proceeding in this case consists in cutting up the organ into shreds, heating it on a water-bath with a fourth of its weight of hydrochloric acid, the mixture being diluted with water till it becomes of the consistency of a thin paste. It may then be subjected to Reinsch's process, or it is fit for trial in Marsh's apparatus. Fresenius and Von Babo (*Liebig's Ann.* xlix. 287) prefer to add to the original mixture of hydrochloric acid and organic matter, small portions of potassic chlorate from time to time until a homogeneous yellow liquid is obtained; when cold it is filtered through linen, the residue well washed, and the clear liquid is concentrated by evaporation by a heat not exceeding that of the water-bath. In this case it is necessary subsequently to reduce the arsenic acid in the liquid to arsenious acid by means of a current of sulphurous acid gas. They then heat gently to expel the excess of sulphurous acid, precipitate the arsenic by sulphuretted hydrogen, collect the

FIG. 359.



precipitate on a small filter, wash, dissolve out the arsenious sesquisulphide with ammonia, evaporate the solution on a watch-

glass, and reduce the sulphide by mixing it with about 12 times its weight of a mixture of 3 parts of dried sodic carbonate and 1 of potassic cyanide, and heating it in a very slow current of dried carbonic anhydride, as shown in fig. 359, in which *a* represents a flask containing fragments of marble from which the carbonic anhydride is disengaged by the addition of hydrochloric acid: *b* contains oil of vitriol in order to dry the issuing gas; the arsenical mixture is placed in the bend of the tube *c*, and the metallic crust is sublimed into the contracted part of the tube at *d*. This process is tedious and complicated, and not superior to Reinsch's if the latter be conducted with due care. A very delicate mode of detecting the presence of arsenic is afforded by the action of the voltaic current, which may be applied without difficulty by adopting the precautions recommended by Bloxam (*Q. J. Chem. Soc.* xiii. 12). The galvanic process has the advantage of being applicable to the detection of various other metallic poisons if arsenic be absent, as nothing is introduced which interferes with their identification subsequently by appropriate tests.

(847) *Estimation of Arsenic*.—It is not easy to ascertain accurately, by analysis, the quantity of arsenic present in a compound; but the following is the plan generally adopted:—The metal is precipitated in the form of a sulphide: the precipitate collected on a weighed filter, dried at  $100^{\circ}\text{C}$ ., and weighed: a given weight of the sulphide is then oxidized by means of nitric acid (sp. gr. 1.51); and when it is completely dissolved, the sulphur is precipitated as baric sulphate. From the weight of this precipitate the quantity of sulphur is calculated, and deducted from the total amount of arsenical sulphide; the difference gives the amount of the metal. The sulphide is apt to contain a variable quantity of free sulphur, and hence this method becomes necessary. Before it can be adopted, the absence of all other metals in the sulphide must, of course, be ascertained. The arsenic acid in the solution may further be precipitated as ammonio-magnesian arseniate, by neutralizing with ammonia, and adding a solution of magnesian sulphate containing ammonic chloride and ammonia in excess: 100 parts of this precipitate dried at  $100^{\circ}\text{C}$ . [ $2(\text{H}_4\text{NMgAsO}_4), \text{H}_2\text{O}$ ] represent 39.47 of metallic arsenic.

(848) *Separation of Arsenicum from other Metals*.—By means of sulphuretted hydrogen and the subsequent solution of the sulphide in ammoniac sulphide, arsenic is easily separated from all the foregoing metals with the exception of those which form soluble compounds with the sulphides of the alkali-metals. A solution of ammoniac sesquicarbonate (free from uncombined ammonia), when digested on the mixed hydrated arsenical and antimonial sulphides, dissolves the arsenical sulphide only, and leaves it on evaporation.

§ IX. ANTIMONY: (Stibium)  $\text{Sb}''' = 122$ . *Sp. Gr.* 6.715;  
*Fusing-pt.* about  $1150^{\circ}$  ( $621^{\circ}\text{C}$ .); *Triad*, as in  $\text{SbCl}_3$ ;  
*sometimes Pentad*, as in  $\text{SbCl}_5$ .

(849) ANTIMONY is a tolerably abundant substance, and is always extracted from its sesquisulphide, though it is frequently



found alloyed with other metals, and is sometimes met with in the native state.

Antimonious sulphide usually occurs in a matrix of quartz, baric sulphate, and limestone. The *crude antimony* of commerce is merely this sesquisulphide freed from the greater part of its earthy impurities. This purification is effected by placing the ore upon the bed of a reverberatory furnace, covered with charcoal-powder. The sulphide melts, the earthy impurities float, and the fluid portion is drawn off into an iron basin, and is afterwards cast into loaves or cakes. If it be desired to extract the metal, the sulphide thus purified is reduced to a coarse powder, and again placed upon the bed of a reverberatory furnace: the temperature may be gradually raised to dull redness, but must be moderated to prevent the mass from entering into fusion: in about 12 hours fumes cease to rise, most of the sulphur is expelled, and a red mixture of antimonious sesquioxide and sesquisulphide remains. During this process copious vapours of sulphurous and arsenious anhydrides are given off, accompanied by a considerable portion of antimonious oxide. It is stated that nearly 20 per cent. of the metal is lost during this operation. The roasted mass is now mixed with about one-sixth of its weight of powdered charcoal, made into a paste with a strong solution of sodic carbonate, and heated in crucibles to bright redness; the metal collects at the bottom in consequence of the reactions illustrated by the following equations:  $\text{Sb}_2\text{S}_3 + 3\text{Na}_2\text{CO}_3 = 3\text{CO}_2 + 3\text{Na}_2\text{S} + \text{Sb}_2\text{O}_3$ , and  $\text{Sb}_2\text{O}_3 + 3\text{C} = 3\text{CO} + \text{Sb}_2$ ; above it is a scoria, consisting chiefly of antimonio-sodic sulphide. This scoria is known in the arts as the *crocus of antimony*. The metal is remelted with the scoria, and is then fit for sale, though it is not pure. 100 parts of sesquisulphide yield about 44 parts of metallic antimony, so that in the whole process about three-sevenths of the antimony are lost.

On the small scale the metal is most easily procured by taking 4 parts of the powdered sesquisulphide, 3 of crude tartar, and  $1\frac{1}{2}$  of nitre, mixing them intimately, and throwing the powder in small portions at a time into a crucible kept at a bright red heat. The quantity of nitre employed is insufficient to oxidize both the sulphur and the metal; and the sulphur being the more combustible element of the two is the first to undergo oxidation, whilst the metal melts and collects at the bottom, beneath the slag of potassic sulphate. Commercial antimony commonly contains arsenicum, iron, and often small quantities of copper and lead.

In order to obtain antimony free from arsenic, Wöhler mixes intimately 4 parts of finely-powdered commercial antimony with 5 of sodic nitrate, and 2 of anhydrous sodic carbonate. The mixture is heated to redness in a Hessian crucible, and the antimony burns quietly at the expense of the oxygen of the nitrate. After the deflagration is complete, the crucible is covered, and the mass

is kept for half an hour at a temperature sufficient to soften but not to fuse it, from time to time pressing it down with an iron spatula. It is removed from the crucible by means of a spatula, while still in a pasty condition, then pulverized and thrown into boiling water: the solution contains the sodic arseniate, while the greater part of the sodic antimoniate remains undissolved, and is well washed with boiling water. From this sodic antimoniate the metal is extracted by melting it with half its weight of crude tartar. The product so obtained is an alloy of antimony with potassium: it is broken into small pieces and thrown into water; a copious disengagement of hydrogen takes place, the potassium is oxidized and dissolved, and the alloy falls to powder. It still retains iron, and sometimes lead. One-third of the mass is converted into oxide by means of nitric acid; this oxide is well washed with water, dried, and then incorporated with the powdered metal; the mass is again melted in a covered crucible, and pure antimony is obtained beneath a layer of fused sesquioxide, which retains the oxides of iron and lead.

(850) *Properties*.—Antimony was well known to the alchemists. It is a brilliant bluish-white metal, of a flaky, crystalline texture, and so brittle that it may readily be reduced to powder. It fuses at about  $1150^{\circ}$  ( $621^{\circ}$  C.), a little above red heat, and by slow cooling may be obtained in rhombohedral crystals, which according to Mitscherlich, are isomorphous with those of arsenicum; but absolutely pure antimony crystallizes with difficulty (Cooke; Matthiessen). The commercial cakes of the metal exhibit upon their upper surface a beautiful penniform crystalline structure. Melted antimony expands in solidifying, the solid metal floating in the melted portion. At a bright red heat it is volatilized slowly: the operation is facilitated by transmitting a current of hydrogen over it. Antimony is inferior to most of the metals as a conductor of heat and of electricity. When exposed, to either a moist or a dry air, at ordinary temperatures, it undergoes no change, but if heated it burns brilliantly, emitting copious white fumes which consist chiefly of antimonious oxide. Powdered antimony takes fire spontaneously when thrown into chlorine gas; bromine and iodine likewise enter into combination with the metal with great evolution of heat, when they are brought into contact with it at ordinary temperatures. It is also oxidized by nitric acid and by boiling sulphuric acid. Aqua regia dissolves it readily. When finely powdered, it is dissolved by strong hydrochloric acid by the aid of heat, with evolution of hydrogen. Metallic antimony, when in fine powder, is readily dissolved by digestion with a solution of one of the higher sulphides of potassium, whilst the lead, iron, copper, bismuth, or silver, which it may contain is left undissolved. Small quantities of arsenicum and of tin, if present, enter into solution with the antimony.

*Alloys*.—Antimony is not used alone in the arts, but it enters

into the composition of several valuable alloys. *Type metal* is one of these: ordinary type is composed of 3 or 4 parts of lead, and 1 part of antimony: but the alloy which is now employed in the best description of type contains 2 parts of lead, 1 of tin, and 1 of antimony. Music type contains tin; and the common white metal used for teapots, under the name of *Britannia metal*, consists of equal parts of brass, antimony, tin, bismuth, and lead. The value of the antimony in these alloys depends upon the hardness which it communicates to them, without rendering them inconveniently brittle, and to the expansion which it confers upon them in the act of solidification, so valuable in the case of type metal. Equal parts of antimony and lead, however, produce a brittle alloy. The compounds of antimony with zinc and with tin are hard, white, and brittle. A mixture of 12 parts of tin, 1 part of antimony, and a small quantity of copper, furnishes a ductile alloy, forming a superior kind of pewter. If lead be substituted for copper in this alloy it is rendered brittle. Antimony also combines readily with copper, furnishing a hard alloy which takes a good polish, but which becomes paler and more brittle in proportion as the quantity of antimony is increased. If 7 parts of powdered antimony and 3 of iron filings be exposed in a covered crucible to a very high temperature, a brittle alloy is formed sufficiently hard to emit sparks when filed.

With zinc, antimony unites to form two definite alloys, which may be prepared by fusing the two metals together in the proper proportions. They may be crystallized by a method similar to that adopted in the case of sulphur by fusion (407). One of these ( $\text{Sb}_2\text{Zn}_3$ ) crystallizes in long acicular prisms, which belong to the oblique prismatic system; it decomposes water rapidly at 100 C. with evolution of hydrogen. The other alloy ( $\text{SbZn}$ ) crystallizes in broad plates which twin together on an octohedral face.

Prof. J. P. Cooke, jun., who has studied these alloys minutely, finds that in each case the crystalline form of the alloy is preserved, although the proportions of the two metals may vary within considerable limits; thus, the form of needles, (which would require, if in atomic proportion,  $\text{Sb}_2\text{Zn}_3$ , a per-centage of 55.7 of antimony), is still preserved, though the antimony may fall as low as 35.77 or may rise as high as 57.24; while the form of plates is observed without any variation in the angular measurements, although the quantity of antimony may fall as low as 64.57 or may rise as high as 79.42, though 65.07 would represent the true atomic proportion ( $\text{SbZn}$ ). It is true both the forms belong to the same crystalline system, but they do not appear to be derivable one from the other. Prof. Cooke suggests that these observations may throw an important light upon the cause of the hitherto unexplained variation in composition occasionally observed in minerals of the same crystalline form, the components of which are not isomorphous; and he proposes the term *Allomerism* to designate such variation in the proportions of the constituents of the crystalline compound without any essential change in the crystalline form, the varying constituents not being isomorphous with each other.

Matthiessen and Von Bose, in their researches upon the alloys of tin and

gold, have found that those containing from 27·4 to 43 per cent. of gold all crystallize in the same form, the largest and best defined crystals containing about 4·1 per cent. of gold ( $\text{AuSn}_2 = 45\cdot9$  per cent. of gold).

In combination with hydropotassic tartrate, antimonious oxide forms a powerful and valuable medicine. The oxide, when ground up with linseed oil, furnishes a pigment which is employed to some extent as a substitute for white lead: it is much less injurious to the health of those who use it than pigments which contain lead.

Mr. Gore (*Phil. Trans.* 1858, p. 185) has described a remarkable modification of antimony which may be procured by electrolytic action, in the following manner:—Dissolve 1 part of tartar-emetic in 4 parts of the solution obtained by dissolving antimonious sulphide nearly to saturation in hydrochloric acid, and subject the solution to the action of two or three cells of Smee's battery, using a plate of antimony for the positive and a copper wire for the negative electrode. A metallic deposit having the colour and lustre of highly-polished steel, with a peculiar mammillated surface and an amorphous structure, is formed. Its specific gravity is about 6·55. The metal thus deposited retains 5 or 6 per cent. of antimonious chloride, and if suddenly struck sharply, or heated, it undergoes a rapid molecular change attended with a rise of temperature amounting sometimes to  $450^\circ$  ( $250^\circ$  C.), accompanied by the disengagement of abundant fumes of antimonious chloride. The heat evolved is sufficient to boil water or even to fuse small pieces of tin. After this change has occurred, the metal is found to retain its cohesion and its metallic aspect, but it has become grey, and acquired a granular fracture and an increased density. A corresponding substance may be obtained if antimonious bromide be substituted in electrolysis for the trichloride, the deposited metal in this case retaining a portion of the tribromide.

(851) OXIDES OF ANTIMONY.—Antimony forms three well-marked oxides: the first is the most important, as it constitutes the basis of the antimonial salts employed in medicine. The oxides have the following composition:—

		Oxygen.	Antimony.
Antimonious oxide	... $\text{Sb}_2\text{O}_3$	= 16·44	+ 83·56
Antimonic anhydride	... $\text{Sb}_2\text{O}_5$	= 24·69	+ 75·31
Antimonious antimoniate	... $\text{Sb}_2\text{O}_3, \text{Sb}_2\text{O}_5$	= 20·78	+ 79·22

*Antimonious oxide*, or *Sesquioxide of antimony*, formerly called the *teroxide* ( $\text{Sb}_2\text{O}_3 = 292$ ).—In the anhydrous state this oxide is found crystallized in prisms in a rare mineral called *white antimony ore*, of specific gravity 5·56. The anhydrous sesquioxide is best procured by boiling powdered metallic antimony to dryness in an iron ladle, with excess of strong sulphuric acid; an insoluble sulphate is formed, and sulphurous anhydride is disengaged. To remove the sulphuric acid, the residue is treated with sodic carbonate and is well washed: the greyish-white insoluble powder which remains is the sesquioxide. When heated it assumes a yellow colour, but recovers its whiteness on cooling. When heated in closed vessels it may be melted; at a

high temperature it may be volatilized, and the vapour may be condensed in brilliant crystalline needles isomorphous with the unusual form of arsenious anhydride. Occasionally it crystallizes in octohedra, like the common variety of arsenious anhydride. In the open air it burns like tinder, and is converted into the so-called antimonious acid. Hydrochloric and tartaric acids dissolve it freely. Nitric acid converts it into one of higher oxides of antimony. With sulphuric acid it forms an insoluble sulphate, though its basic properties are but feeble. In the hydrated state it may be obtained by pouring a solution of antimonious chloride into an excess of a solution of sodic carbonate. In this form it is readily soluble in solutions of caustic potash and soda; but the simple ebullition or evaporation of the liquid causes a separation of antimonious oxide in prismatic crystals.

(852) *Antimonic anhydride*, formerly *Antimonic acid* ( $\text{Sb}_2\text{O}_5 = 324$ ).—This compound may be obtained by oxidizing the metal with nitric acid, and expelling the excess of nitric acid by a heat below redness. It is of a pale yellow colour, is tasteless, and insoluble in water. A strong heat expels one-fifth of its oxygen, and converts it into antimonious antimoniate ( $\text{Sb}_2\text{O}_4$ ), which is a white powder, formerly termed *antimonious acid*, but which possesses no acid characters; for if treated with hydropotassic tartrate (cream of tartar) it is decomposed, antimonio-potassic tartrate (*tartar-emetica*) being formed, whilst antimonic anhydride is left ( $2\text{Sb}_2\text{O}_4 = \text{Sb}_2\text{O}_3 + \text{Sb}_2\text{O}_5$ ).

*Antimoniates*.—Antimonic acid forms definite compounds with the metals of the alkalis: a boiling solution of caustic potash dissolves it, and on the addition of an acid, the liquid deposits hydrated antimonious acid in the form of a white powder ( $\text{Sb}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ ), which reddens litmus, and is freely soluble in cold solutions of the alkalis, and in hydrochloric acid. Fremy states that antimonic acid may, like hydrated stannic dioxide, be obtained in two modifications, each of which combines with different amounts of base, and forms a distinct class of salts: to one of these modifications, obtained by treating metallic antimony with nitric acid, he gives the name of *antimonic acid*; its normal potassic salt has the formula ( $\text{K}_2\text{Sb}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ , or  $\text{K}_2\text{O} \cdot \text{Sb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ ): the other modification procured by decomposing antimonic pentachloride with water, he terms *metantimonic acid*. To the normal potassic salt of the latter acid, he assigns the composition indicated by the formula ( $2\text{K}_2\text{O} \cdot \text{Sb}_2\text{O}_5$ , or  $\text{K}_4\text{Sb}_2\text{O}_7$ ).

According to Fremy, antimonious acid is monobasic, but it is capable of forming both normal and acid salts. The normal antimonates are gelatinous and uncrystallizable. *Normal potassic antimonate* may be procured by heating 1 part of metallic antimony with 4 parts of nitre in an earthen crucible. The white mass so obtained is powdered, and washed with warm water, to remove the excess of potash and potassic nitrite. The residue must be boiled in water for an hour or two; the *insoluble anhydrous* antimonate is thus converted into a *soluble* hydrated modification consisting of  $\text{K}_2\text{Sb}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ . The insoluble residue now consists chiefly of acid-antimonate of potassium. The normal salt

possesses the property of freely dissolving the acid-antimoniate, which is precipitated when such a solution is mixed with any neutral salt of one of the alkalis. The normal antimoniate does not crystallize, but forms a gummy mass which has an alkaline reaction; it is readily decomposed by acids, including the carbonic, whilst the acid-antimoniate is deposited. When heated to  $320^{\circ}$  ( $160^{\circ}$  C.) it loses 2 out of its 5 atoms of water, and becomes insoluble in cold water.

*Acid-antimoniate of potassium* ( $K_2Sb_4O_{11}$ ), or *Dipotassic diantimoniate* ( $K_2O, 2Sb_2O_3$ ), is obtained by transmitting a current of carbonic anhydride through a solution of the normal antimoniate. It is quite insoluble in water, but is soluble in a hot solution of the normal antimoniate, and is deposited in crystals as the liquid cools.

If antimonie anhydride be heated with plumbic oxide it combines with it and yields a yellow compound, which is used as a pigment under the name of *Naples yellow*.

(853) *Metantimonic acid* ( $H_4Sb_4O_7$ , or  $2H_2O, Sb_2O_3$ ). This compound derives its principal interest from the circumstance of its yielding a soluble compound with potassium, which may be employed as a test for sodium. The metantimonates of the alkalis are crystallizable. The *acid-metantimoniate of potassium*,  $K_2H_2Sb_4O_7, 6H_2O$ , or *hydropotassic metantimoniate*, is the salt which is used for this purpose. In preparing this compound, potassic antimoniate is first formed by deflagrating antimony with nitre, washing and boiling the residue in the manner already described, so as to bring the whole of the normal antimoniate into solution: the liquid thus obtained is filtered, and evaporated to a syrupy consistence in a silver dish; fragments of caustic potash are then added, and the evaporation is continued until a drop of the liquid placed upon a cold slip of glass begins to crystallize; it is then allowed to cool, and the alkaline supernatant liquid is poured off the crystals, which are allowed to drain upon a porous tile. When the salt is required as a test for salts of sodium, 30 or 40 grains (2 or 3 grammes) of this residue are to be washed quickly with about twice their weight of cold water, and allowed to subside; this washing is to be repeated two or three times, in order to remove traces of adhering potash; lastly, a little cold water is to be digested for a few minutes upon the residue, and the filtered liquid may be used to ascertain the presence of sodium. The presence of potassic hydrate impairs the delicacy of the reaction. One great inconvenience which attends the use of this reagent is the circumstance, that if the solution be kept for a few days, the salt passes spontaneously into the normal antimoniate, and this salt does not precipitate the compounds of sodium; both salts contain exactly the same amount of acid and of base ( $K_2H_2Sb_4O_7 = K_2Sb_2O_5, H_2O$ ), the difference in properties being due to difference in the molecular constitution of the two salts. If the solution of the acid metantimoniate be boiled, its conversion into normal antimoniate is effected in a few minutes. The *acid sodic metantimoniate* ( $Na_2H_2Sb_4O_7, 6H_2O$ ) is an insoluble salt, which crystallizes in octahedra.

(854) *ANTIMONIURETTED HYDROGEN* ( $H_2Sb?$ )—The composition of this gas is not known with certainty, for at present it has never been obtained free from hydrogen. It is inferred, however, to contain 3 atoms of hydrogen to one atom of the metal, because, when transmitted through a solution of argentic nitrate, a precipitate of triargentic antimonide is formed ( $Ag_3Sb$ );  $3AgNO_3 + H_2Sb$  becoming  $3HNO_3 + Ag_3Sb$ . Antimoniuretted hydrogen is formed by dissolving an alloy of zinc and antimony in diluted sulphuric acid. When a solution of any antimonious salt is

poured into a mixture of zinc and sulphuric acid which is disengaging hydrogen, the antimonial salt becomes decomposed; one portion of the antimony is deposited in the form of a black powder upon the surface of the zinc, whilst another portion combines with the hydrogen, and assumes the gaseous state. It forms a colourless gas which is without any marked odour. When burned, it deposits white fumes of antimonious oxide, and if transmitted through a glass tube, heated to low redness, the gas is decomposed, and the antimony forms a brilliant metallic crust upon the heated portion of the tube.

(855) **SULPHIDES OF ANTIMONY.**—Two compounds of antimony with sulphur are known; the ordinary sesquisulphide ( $\text{Sb}_2\text{S}_3$ ), and the antimonious sulphide ( $\text{Sb}_2\text{S}_5$ ), corresponding to the antimonious sesquioxide and to antimonious anhydride. They are usually regarded as sulphur-acids, since they combine with the sulphides of the alkali-metals, and form definite salts.

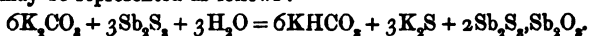
*Antimonious sulphide, or Sesquisulphide of antimony*,  $\text{Sb}_2\text{S}_3 = 340$ ; *Sp. Gr.* 4.626; *Comp. in 100 parts*, Sb, 71.76; S, 28.24.—This substance constitutes the only ore from which the metal is obtained. The native sesquisulphide, or *grey antimony ore*, is usually found in granite or slate rocks, and generally contains lead and arsenic, besides a variable amount of pyrites. It occurs crystallized in four-sided prisms, striated transversely; it has a bluish-black colour, and a strong metallic lustre. It is friable, and melts below a red heat, crystallizing as it cools. It may be distilled unchanged in closed vessels, at a very high temperature, but by roasting in the open air it is converted into a fusible mixture of antimonious sesquioxide and sesquisulphide. This oxy-sulphide, after it has been fused, constitutes the commercial *glass of antimony*, which contains about 8 parts of the sesquioxide to 1 part of sesquisulphide. If the sesquioxide be in excess, the glass is transparent, and of a fine red colour: the greater the proportion of the sesquisulphide, the darker is the tint. The glass attacks the silica of the crucible in which the fusion is performed, and dissolves a considerable portion of it. A native *oxysulphide of antimony* ( $\text{Sb}_2\text{O}_3, 2\text{Sb}_2\text{S}_3$ , known as *red antimony ore*) occurs crystallized in oblique rhombic prisms.

Antimonious sulphide may be obtained in crystals by melting together, at a red heat, a mixture of sulphur and the sesquioxide; sulphurous anhydride escapes, and antimonious sulphide is formed:  $2\text{Sb}_2\text{O}_3 + 9\text{S}$  becoming  $2\text{Sb}_2\text{S}_3 + 3\text{SO}_2$ .

Attempts have been recently made, with some success, to introduce the artificial sesquisulphide as a red pigment, under the name of *antimony vermilion*.

The colour is prepared by pouring a crude solution of antimonious chloride in hydrochloric acid into a dilute solution of calcic hyposulphite, which is maintained in excess; on heating the liquid to  $140^{\circ}$  ( $60^{\circ}$  C.), it becomes turbid, and deposits a precipitate which is at first yellow and ultimately a bright orange red. The anhydrous sesquisulphide may also be obtained of a beautiful orange colour, by transmitting sulphuretted hydrogen through a solution of any salt of the metal: on being heated in closed vessels, it assumes a dark metallic appearance, resembling that of the native sulphide. If heated in a current of hydrogen gas, the sulphur is removed and metallic antimony is left. The sesquisulphide, whether artificial or native, is dissolved by hot hydrochloric acid, and furnishes a convenient source of pure sulphuretted hydrogen, provided that the gas be washed, to free it from traces of antimony and hydrochloric acid which it is apt to retain in suspension.

Antimonious sulphide is readily soluble in solutions of the sulphides of the alkali-metals, and forms colourless compounds, which have been regarded as double sulphides, or *sulphantimonites*; a hot solution of the alkaline sulphide can dissolve much more of the sesquisulphide than it can retain when cold; on the addition of an acid, the sulphide of the alkali-metal is decomposed, and the antimonious sulphide is reprecipitated. If the sesquisulphide in fine powder be boiled with a solution of potassic carbonate, or of caustic potash, it is dissolved; the filtered liquid on cooling deposits a reddish-brown substance, known as *kermes mineral*. This substance is not a definite compound, but is a variable mixture of antimonious sesquisulphide and sesquioxide, the latter being combined with a small portion of the alkali. The action of potassic carbonate on the sesquisulphide may be represented as follows:—



In this mixture of  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{O}_3$ , H. Rose found crystals of antimonious oxide, which were visible by the aid of the microscope. Cream of tartar, or diluted hydrochloric acid, dissolves out the sesquioxide, leaving the sesquisulphide. If to the liquid, after deposition of the kermes, hydrochloric acid be added, effervescence takes place, with escape of sulphuretted hydrogen, owing to the decomposition of dipotassic sulphide, and the excess of antimonious sulphide which it retained is precipitated as the *golden sulphide of antimony*. This sulphide contains a larger proportion of sulphur than the sesquisulphide, from the gradual oxidation of the antimony in the solution before the precipitation is effected.

*Antimonic sulphide* ( $\text{Sb}_2\text{S}_5 = 4.04$ ; *Comp. in 100 parts*, Sb, 60.4; S, 39.6), or *Sulphantimonic acid*, as this compound is often termed, may be obtained by transmitting a current of sulphuretted hydrogen through an acid solution of antimonic pentachloride. It forms an orange-yellow precipitate, which is anhydrous, but is remarkable for the facility with which it combines with the sulphides of the alkali-metals. The trisodic *sulphantimoniate* ( $\text{Na}_3\text{SbS}_4\cdot\text{OH}_2$ ), or Schlippe's salt, crystallizes in large and very brilliant transparent tetrahedra. It may be obtained in various ways: the easiest plan consists in thoroughly mixing 18 parts of finely-powdered antimonious sulphide, 12 of dried sodic carbonate, 13 of quicklime, and  $3\frac{1}{2}$  of sulphur; the mixture is ground up with water, and placed in a well-closed bottle, which is completely filled with water; it is allowed to digest, with frequent agitation, for 24 hours; the clear liquid is filtered off, and allowed to evaporate spontaneously in a closed vessel over sulphuric acid. This salt when mixed with an acid deposits pure antimonic sulphide. The moist crystals when exposed to the air absorb carbonic acid and become brown.

(856) **CHLORIDES OF ANTIMONY.**—Antimony has a powerful attraction for chlorine. It forms two chlorides,  $\text{SbCl}_3$  and  $\text{SbCl}_5$ : they correspond in composition with the oxides and sulphides.



*Antimonious chloride*, or *Trichloride of antimony* ( $\text{SbCl}_3 = 228.5$ ); *Spr Gr. of Liquid*, at  $73^\circ \text{C.}$ , 2.676; *of Vapour*, 7.8; *Fusing-pt.*  $161^\circ.6$  ( $72^\circ \text{C.}$ ); *Mol. Vol.* [ ] ; *Rel. wt.* 114.25; *Boiling-pt.*  $433^\circ.4$  ( $223^\circ \text{C.}$ ).—This substance, from its ready fusibility, was formerly known under the name of *butter of antimony*. It may be obtained in the anhydrous form by distilling an intimate mixture of 8 parts of corrosive sublimate with 3 of powdered metallic antimony; calomel, antimonious trichloride, and an amalgam of antimony are formed;  $2\text{Sb} + 2\text{HgCl}_2 = \text{SbCl}_3 + \text{SbHg} + \text{HgCl}$ . Antimonious chloride may be more cheaply prepared by mixing antimonious sulphate with twice its weight of sodic chloride, and then distilling the mixture. It may also be obtained by distilling the residue left on dissolving antimonious sulphide in hydrochloric acid. The trichloride is a volatile, fusible, crystallizable compound, which is deliquescent, and powerfully corrosive in its action on animal tissues; it is soluble in hydrochloric acid, and in a small quantity of water: but if thrown into a large mass of water an insoluble oxychloride ( $\text{SbCl}_2, \text{Sb}_2\text{O}_3$ ) falls, which gradually assumes a compact crystalline form; it was formerly called *powder of algaroth*. On diluting a hot solution of antimonious chloride in hydrochloric acid with hot water, it deposits, on cooling, brilliant needles, which may be represented as  $(2\text{SbCl}_3, 5\text{Sb}_2\text{O}_3)$ . By heat, the trichloride is sublimed, leaving the sesquioxide. Antimonious chloride is used for bronzing gun-barrels, in order to prevent them from rusting.

*Antimonic chloride*, or *pentachloride* ( $\text{SbCl}_5 = 299.5$ ) is prepared by exposing powdered antimony, gently heated in a retort, to a current of dry chlorine in excess. It forms a volatile, colourless liquid, which emits dense, suffocating white fumes when exposed to the air. With a small quantity of water it forms white, deliquescent crystals; but it is decomposed by a large quantity of water, and metantimonic acid, which retains a little hydrochloric acid, is deposited:  $2\text{SbCl}_5 + 7\text{H}_2\text{O} = \text{H}_4\text{Sb}_2\text{O}_7 + 10\text{HCl}$ . Dry antimonic chloride absorbs sulphuretted hydrogen, and forms with it a white crystalline fusible solid ( $\text{SbCl}_5\text{S}$ ), which corresponds in composition to phosphoric chlorosulphide. Both the antimonial chlorides form definite compounds with ammonia. The pentachloride is sometimes used as a chlorinating agent, since it readily parts with a portion of its chlorine to many compounds of organic origin which contain hydrogen.

*Antimonious bromide* ( $\text{SbBr}_3$ ), or the *tribromide*, is a colourless crystalline solid. The *tri-iodide* is a solid of a red colour. *Tartar-etic*,  $2[\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6]\text{H}_2\text{O}$ , is an important salt of antimony, which is used in medicine; it will be described hereafter with the other tartrates.

(857) **CHARACTERS OF THE COMPOUNDS OF ANTIMONY.**—According to Péligot (*Ann. de Chimie*, III. xx. 297), antimonious oxide, by its reaction with acids, forms salts which contain 1, 2, or 4 equivalents of a monobasic acid radicle. Most of them when largely diluted with water become milky from the deposition of a

basic salt of sparing solubility; but this milkiness disappears on the addition of tartaric acid, or of hydropotassic tartrate. They are all of them colourless, and when taken internally in large doses produce poisonous effects. Infusion of cinchona bark yields a copious insoluble precipitate with antimonial salts, and it has been recommended to administer this medicine in cases of poisoning with antimony: it is not, however, to be relied on.

Except when tartaric acid is present, the *caustic alkalies* give, with antimonial salts, a white precipitate soluble in excess of the alkali; *ammonia* and the *carbonates of the alkalies*, a white precipitate nearly insoluble in excess. But the characteristic reaction of these salts when in solution is the formation of an orange-coloured precipitate of antimonious sulphide, when their solutions, acidulated with hydrochloric acid, are acted on by *sulphuretted hydrogen*; this precipitate is soluble in ammoniac hydrosulphide. In detecting antimony for medico-legal purposes, antimoniuiretted hydrogen is first prepared, and subsequently decomposed by heat. In order to effect this, the suspected liquid, after boiling with hydrochloric acid and a little potassic chlorate, is filtered and introduced into Marsh's apparatus; the experiment is then proceeded with as directed for arsenic (846). A more delicate method is the following:—The suspected solution is acidulated with hydrochloric acid, and boiled with a slip of bright copper foil, which becomes coated with a violet-coloured film of reduced antimony: when heated, with the precautions directed in applying Reinsch's test for arsenic (p. 667), the antimony gradually becomes oxidized, and at a high temperature the oxide is volatilized, condensing in needles, not, like that of arsenic, in octohedra; but the metal may be identified by heating the slip in a tube with a solution of pure potassic hydrate, exposing the surface of the metal freely to the air; the antimony is gradually oxidized and dissolved. The solution should next be somewhat diluted, submitted to the action of sulphuretted hydrogen, filtered from any sulphide of copper or lead, and then on the addition of hydrochloric acid in slight excess the antimony is precipitated as sesquisulphide in characteristic orange flocculi. This precipitate may be dissolved in hydrochloric acid, and will then give a crust of metallic antimony if introduced into Marsh's apparatus.

(858) *Estimation of Antimony*.—In determining the quantity of this metal, the solution is first acidulated with a mixture of hydrochloric and tartaric acids, then subjected to a current of sulphuretted hydrogen, and exposed for a few hours in an open, shallow dish, at a temperature not exceeding  $104^{\circ}$  ( $40^{\circ}$  C.): the excess of sulphuretted hydrogen is thus got rid of, and the whole of the antimony is separated as sesquisulphide, but the weight of the dried precipitated sesqui-

sulphide cannot be relied upon as furnishing a correct datum for estimating the metal, because it is liable to contain a variable excess of uncombined sulphur. It must therefore be dried at  $100^{\circ}\text{C}$ ., and weighed; a certain proportion of it is then dissolved in hot aqua regia, after which the solution is mixed with a little tartaric acid; and the sulphur, which has by this means been converted into sulphuric acid, is precipitated by the addition of baric chloride: the sulphur is calculated from the weight of the baric sulphate obtained, and deducted from the weight of antimonious sulphide employed; the difference is estimated as antimony. According to Bunsen, the sulphide may be converted into the so-called antimonious acid ( $\text{Sb}_2\text{O}_3$ ), in which form it may be weighed, by proceeding as follows:—Place the sulphide in a counterpoised porcelain capsule, with a concave cover, moisten it with red concentrated nitric acid, and evaporate to dryness by the aid of a water-bath: the white mass of antimonious sesquisulphate, which is left, is converted by ignition into antimonious acid, 100 parts of which correspond to 79.22 of the metal. The oxidation of the antimonial sulphide may also be effected by mixing it intimately with 40 or 50 times its weight of mercuric oxide, and simply igniting the mixture in a covered crucible until it ceases to lose weight; sulphurous anhydride and metallic mercury are expelled, and antimonious acid is left as before. If the precipitate contain a large excess of sulphur, it may be digested with carbonic disulphide before proceeding to the oxidation. Antimony may be separated, by means of sulphuretted hydrogen, from all the metals previously described, with the exception of cadmium, tin, tungsten, molybdenum, and arsenicum. Cadmic sulphide is not soluble in ammoniac hydro-sulphide, whilst that of antimony is soluble; this liquid may therefore be employed to separate these metals.

(859) In order to *separate arsenic from antimony*, the mixed sulphides are digested in a solution of ammoniac sesquicarbonate containing no free ammonia: this solvent takes up the arsenious sulphide, and dissolves scarcely any antimonious sulphide.

The *separation of antimony from tin* in a metallic alloy may be effected with tolerable accuracy, by dissolving the alloy in hydrochloric acid, which is to be mixed with a small proportion of nitric acid, in order to prevent loss of antimony as antimoniu-retted hydrogen. The two metals are then precipitated together by means of metallic zinc, and the pulverulent metals are dried at  $100^{\circ}\text{C}$ . and weighed. This precipitate is redissolved in weak aqua regia, and is digested at a gentle heat upon a bar of tin, which throws down antimony only. The precipitated metal is collected, washed, dried, and weighed.

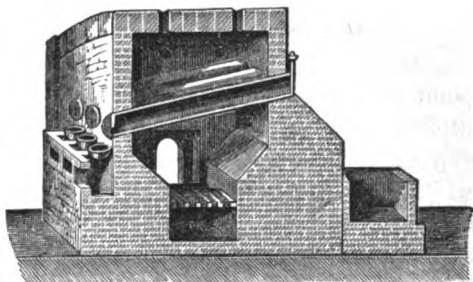
§ X. BISMUTH: ( $\text{Bi}''' = 210$ .) *Sp. Gr.* 9.799;

*Fusing-pt.*  $507^{\circ}\cdot 2$  ( $264^{\circ}\text{C}$ .).

(860) BISMUTH is not an abundant metal; it occurs generally in the native state in quartz rock, and is extracted from its matrix by simple fusion, the mineral being usually heated in iron tubes, which are placed across the furnace in an inclined position; the ore is introduced at the upper end, and the melted metal is drawn off into iron basins below, by opening a plugged aperture at intervals. Fig. 360 shows a section of the furnace used at Schnee-berg in this operation, where the bismuth is extracted from an ore rich in cobalt. Occasionally it is found as a sesquioxide, or as a sesquisulphide, and sometimes it is met with combined with

tellurium. It generally contains silver, which may be extracted by cupellation. Its mines occur for the most part in Saxony, Transylvania, and Bohemia. Commercial bismuth is never pure: it is apt to contain a little sulphur and arsenic, which may be got rid of by fusing the metal with about one-tenth of its weight of nitre; but it still retains silver, lead, and iron. It may be ob-

FIG. 360.



tained free from these impurities by solution in nitric acid: the acid liquid when saturated with the metal is allowed to become clear, and is poured into a large bulk of water. A sparingly soluble basic bismuth nitrate is thus precipitated; it is washed, dried, and reduced in a crucible by ignition with one-tenth of its weight of charcoal: pure bismuth collects at the bottom.

*Properties.*—Bismuth is a hard, brittle metal, of a reddish-white colour; it fuses at  $507^{\circ}\cdot 2$  ( $264^{\circ}$  C.), according to Rudberg (or  $512^{\circ}\cdot 6$  [ $267^{\circ}$  C.], Person), and it expands considerably at the moment of congelation; when pure it may be obtained by slow cooling after fusion (72) crystallized in large cubes,\* which are frequently hollow. Marchand and Scheerer found that the density of bismuth was diminished by powerful compression, probably owing to the formation of minute internal fissures; they thus reduced it from 9.799 to 9.556. Bismuth is slightly volatile when strongly heated. It is but little altered by exposure to the air at ordinary temperatures, but is rapidly oxidized if exposed to the air at a red heat; if thrown in powder into chlorine it takes fire: it also unites easily with bromine, with iodine, and with sulphur. Hydrochloric acid has little action on it. Boiling sulphuric acid oxidizes it with evolution of sulphurous anhydride; but its proper solvent is nitric acid, which oxidizes and dissolves it rapidly.

*Uses.*—The applications of bismuth are but limited; it is occasionally employed instead of lead in cupellation; some of its compounds are used as pigments, and the basic nitrate is employed medicinally. Its most remarkable alloy is that known as *fusible*

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\* The crystals of bismuth, however, belong to the rhombohedral system, as they are not true cubes, but rhombohedra, the angles of which are within  $2^{\circ} 20'$  of right angles.

*metal.* This is composed of 2 parts of bismuth, 1 of lead, and 1 of tin, or 2 atoms of bismuth, 1 of lead, and 2 of tin. The mixture fuses at a little below  $100^{\circ}$  C., and passes through a pasty condition previous to complete fusion. It dilates in an anomalous manner, when exposed to heat; according to Erman it expands regularly from  $0^{\circ}$  C. to  $35^{\circ}$ , then contracts gradually to  $55^{\circ}$ , at which point it occupies a less bulk than it did at  $0^{\circ}$ ; it then expands rapidly till it reaches  $80^{\circ}$  C., and from that point till it melts its expansion is uniform. This faculty of expanding as it cools, while still in the soft state, renders the alloy very valuable to the die sinker, who employs it to test the perfection of his die,—every line being faithfully reproduced on taking a cast. The addition of cadmium to this alloy depresses its fusing-point still further (716).

Bismuth increases the fusibility of those metals with which it is alloyed to a remarkable extent.

(861) **OXIDES OF BISMUTH.**—Bismuth forms two principal oxides: a sesquioxide ( $\text{Bi}_2\text{O}_3$ ), and an acid oxide or anhydride ( $\text{Bi}_2\text{O}_5$ ); besides these there is a compound oxide ( $\text{Bi}_2\text{O}_4$ ), formed by the union of the two preceding combinations. A bismuthous oxide ( $\text{BiO}$ ) of a velvet-black colour may also be obtained (Schneider) by treating equivalent quantities of bismuth chloride and stannous chloride with an excess of caustic potash, filtering and drying in a current of carbonic anhydride: it burns into the sesquioxide when heated in the air.

*Bismuth oxide, or Sesquioxide of bismuth* ( $\text{Bi}_2\text{O}_3=468$ ); *Sp. Gr.* 8.211; *Comp. in 100 parts*, Bi, 89.74; O, 10.26.—This compound may be obtained in the anhydrous form, by heating the nitrate or the basic nitrate of the metal to low redness. It is a yellow, insoluble powder, which fuses at a red heat, and is easily reduced to the metallic state by heating it with charcoal. A white hydrate of this oxide ( $\text{Bi}_2\text{O}_3, \text{H}_2\text{O}$ ) may also be procured by precipitating a salt of bismuth by an excess of ammonia.

*Bismuthic anhydride* ( $\text{Bi}_2\text{O}_5=500$ ), or *Peroxide of bismuth*, may be procured by digesting the washed hydrated sesquioxide in a concentrated solution of potash, and transmitting chlorine gas. A blood-red solution of potassic bismuthate is thus obtained, and a red precipitate is formed, which is to be well washed, and then digested in cold nitric acid to remove the bismuth oxide with which it is always mixed. A red powder is thus left, which is bismuthic acid ( $\text{HBiO}_3$ ); by a heat of  $269^{\circ}.6$  ( $132^{\circ}$  C.) it is rendered anhydrous, and assumes a brown colour. At a somewhat higher temperature it loses oxygen, and becomes converted into the intermediate oxide, or bismuth bismuthate. According to Arppe, more than one of these intermediate oxides may be formed. Bismuthic acid forms salts with the alkali-metals, but these compounds are decomposed by mere washing with water. The acid is decomposed by concentrated sulphuric acid at

ordinary temperatures, and by nitric acid if the temperature be raised, oxygen being expelled and a salt corresponding to bismuth oxide formed.

(862) **BISMUTH SULPHIDE**, or *Sesquisulphide of bismuth* ( $\text{Bi}_2\text{S}_3=516$ ), occurs native as *bismuth glance* in delicate needles, and in crystals isomorphous with those of native antimonious sulphide. It may be formed artificially by fusing the metal with sulphur: a fusible dark grey compound, with a feebly metallic lustre, is thus obtained; in closed vessels it is decomposed into a subsulphide, and into free sulphur, which distils; in the open air sulphurous anhydride escapes, and bismuth oxide remains. When solutions of bismuth are treated with sulphuretted hydrogen, a black precipitate of the sesquisulphide is formed. Bismuth sulphide is dissolved by the metal in all proportions, a circumstance which affords an easy method of obtaining it in crystals, since the sesquisulphide crystallizes at a temperature at which the metal still remains fluid.

(863) **BISMUTH CHLORIDE**, or *Trichloride of bismuth* ( $\text{BiCl}_3=316.5$ ; *Sp. Gr. of vapour*, 11.16; *of solid*, 4.56; *Mol. Vol.*  $\square$ ; *Rel. wt.* 158.25), may be obtained by heating bismuth with chlorine, or by mixing the metal in fine powder with twice its weight of corrosive sublimate, and distilling. It is a very fusible, volatile, deliquescent compound; but is decomposed by a large quantity of water into free hydrochloric acid, and bismuth oxychloride [ $2(\text{BiCl}_3, \text{Bi}_2\text{O}_3), \text{H}_2\text{O}$ ], known under the name of *pearl white*. This compound is insoluble in tartaric acid, in solution of potash, and in ammoniac hydrosulphide, characters which distinguish it from the corresponding compound of antimony.

**BISMUTH IODIDE**, or *Tri-iodide of bismuth* ( $\text{BiI}_3$ ; *Sp. Gr.* 5.652), is obtained by heating in closed vessels 6 parts of bismuth with 11 of iodine; it sublimes in six-sided, brilliant plates. It is readily fusible, is of a dark-brown colour, and is insoluble in water; but it forms soluble compounds with hydrochloric acid, and with potassic iodide.

(864) **Bismuth nitrate**, or *Nitrate of bismuth* ( $\text{Bi}_3\text{NO}_9, 5\text{H}_2\text{O}=396+90$ ); *Sp. Gr.* 2.376.—This salt is the only other soluble compound of bismuth of any importance, and is easily procured by dissolving the metal in nitric acid: it may be crystallized from the acid solution in large transparent prisms. If the solution, not too strongly acid, be largely diluted with water, an acid salt remains in the liquid, and a *subnitrate* falls ( $\text{Bi}_2\text{O}_3, 2\text{HNO}_3$ ), called by the old writers *magistery of bismuth*: another basic nitrate ( $\text{Bi}_2\text{O}_3, \text{HNO}_3$ ) is also known. These basic nitrates appear to lose acid by washing.

(865) **CHARACTERS OF THE SALTS OF BISMUTH.**—Bismuth when in solution presents characters less marked than many metals. Its salts are colourless unless the acid be coloured; they are poisonous in large doses; its solutions have an acid reaction;

when diluted they become milky, owing to the formation of sparingly soluble basic salts, unless a large excess of acid be present. *Iron, zinc, copper, and tin* throw down bismuth from its solutions in the metallic state. The hydrated *alkalies* give a white precipitate of the hydrated sesquioxide, which is insoluble in excess of the precipitant, and becomes yellow by boiling it with the liquid. Solutions of the *carbonates, phosphates, tartrates, and ferrocyanides* give white precipitates with its salts. Bismuth phosphate is insoluble in diluted nitric and acetic acids, and it has in consequence been proposed by Chancel as a convenient form in which phosphoric acid may be precipitated from acid solutions (448). This phosphate is, however, largely soluble in hydrochloric acid, whilst if sulphuric acid is present the precipitate generally becomes contaminated with basic bismuth sulphate. *Sulphuretted hydrogen* throws down a black bismuth sulphide, which is insoluble in ammoniac hydrosulphide. *Potassic chromate* gives a yellow precipitate of bismuth chromate, which is insoluble in caustic potash, but freely soluble in diluted nitric acid; it is thus distinguished from plumbic chromate. *Before the blowpipe* its salts are easily reduced on charcoal, and yield a brittle bead of bismuth, around which the yellow oxide is deposited.

(866) *Estimation of Bismuth.*—Bismuth is estimated in the form of bismuth oxide ( $\text{Bi}_2\text{O}_3$ ), 100 parts of which correspond to 89.74 of the metal. Ammoniac sesquicarbonate is its best precipitant, but the solution must not contain any chloride or hydrochloric acid, as an oxychloride of bismuth would in that case be precipitated, and a portion of the bismuth would be volatilized with the chlorine on ignition; the metal must in such a case be precipitated in the form of sesquisulphide. It may be separated from the alkalies, from titanium, and from all the metals of the first four groups (with the exception of cadmium), by means of sulphuretted hydrogen; the solution having been first acidulated with acetic acid. From tin, and from the metals of the fifth group, it may be separated by digesting the mixed sulphides (obtained by transmitting sulphuretted hydrogen through the liquid), in ammoniac hydrosulphide, which leaves the bismuth sulphide, and dissolves the other sulphides. The sesquisulphide must be dissolved in nitric acid, and precipitated by ammoniac sesquicarbonate, which after standing for a few hours throws down the whole of the bismuth in the form of carbonate: it must be ignited in a porcelain crucible; carbonic anhydride is thus expelled, and bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) remains.

Bismuth may be separated from cadmium by the addition of ammonia in excess to the solution of the sulphides in nitric acid; the cadmium is retained in solution, whilst the bismuth is precipitated.

## CHAPTER XVIII.

## GROUP VII.—COPPER, LEAD, THALLIUM, AND INDIUM.

Metals.	Symbol.	Atomic weight.	Atomic vol.	Specific heat.	Fusing point.		Specific gravity.	Electric conductivity ° C.
					° C.	° F.		
Copper ...	Cu	63·5	7·10	0·0951	1091	1996	8·952	99·95
Lead ...	Pb	207·0	18·24	0·0314	325	617	11·36	8·32
Thallium ...	Tl	204·0	17·20	0·0325	294	561	11·862	9·16
Indium ...	In	72·0	...	...	...	...	7·362	...

THESE metals have no close chemical relationship. Thallium is a monad, and resembles silver in its specific heat, but is more like lead in physical properties and in its compounds.

§ I. COPPER: (Cuprum)  $\text{Cu}'' = 63·5$ . *Sp. Gr. from 8·921 to 8·952*; *Fusing-pt.*  $1996^{\circ}$  ( $1091^{\circ}$  C.); *Monad in Cupreous salts*, as  $\text{CuCl}$ ; *Dyad in Cupric salts*, as  $\text{CuCl}_2$ .

(867) THE ORES of copper are numerous. The metal is frequently found native, crystallized in cubes, octohedra, or dendritic crystals; or else in masses, as in the North American and Siberian mines. In the neighbourhood of Lake Superior there is a vein of massive native copper, associated with silver; this vein is in many parts two feet, or 0·6 metre, in thickness. The most common ore of copper, however, is the copper pyrites, or double sulphide of copper and iron ( $\text{Cu}_2\text{S}, \text{Fe}_2\text{S}_3$ ), which occurs in the primitive rocks, and especially in the *killas*, or clay-slate. More rarely the pure cupreous sulphide ( $\text{Cu}_2\text{S}$ ) is found in the mines of Cornwall and of the Ural Mountains. Other less abundant ores are the blue and green carbonates, and the red and black oxides of copper.

The Cornish mines furnish more than a third of the copper which is smelted in Great Britain, but considerable supplies of ore are received from Chili, Cuba, South Australia, and Spain. The most important seat of the copper smelting is Swansea, which sends forth annually from 18,000 to 20,000 tons of the refined metal. North America and Saxony supply the larger portion of the remainder. The Australian ore consists chiefly of the green and blue carbonate in a siliceous matrix; these ores contain from 25 to 35 per cent. of copper. Cuba furnishes both the oxides and the sulphides of the metal. Many of the ores from Chili are



valuable on account of the large proportion of silver which they contain. The Cornish copper pyrites usually occurs (mixed with small quantities of stannic oxide and arsenical pyrites) in a matrix of quartz, fluor-spar, and clay.

(868) *Extraction*.—The main object in the treatment of such an ore as the Cornish, is to oxidize and remove the sulphur and arsenic in the form of sulphurous and arsenious anhydrides, and to get rid of the quartz and oxide of iron in the form of a fusible slag, composed of silicate of iron combined with other earthy impurities, leaving metallic copper free from admixture.

After the ore has been raised from the mine it is sorted; the purest portions are broken into small pieces of the size of a hazelnut, and the earthy portions are crushed and sifted, as in washing tin ore. The English ore is usually so mixed that it may contain an average of  $8\frac{1}{2}$  per cent. of copper.

The theory of copper smelting as practised at Swansea, like that of many other operations in the arts, is simple, though the working details have the appearance of being complicated.\* The principal processes may, however, be enumerated as follows:—

1. Calcining the ore.
2. Melting and granulating for coarse metal.
3. Calcination of the coarse metal.
4. Melting for fine metal.
5. Roasting of the fine metal.
6. Refining and toughening.

We shall make a few remarks upon each of these processes in succession.

(869) 1. *Calcining the Ore*.—The calcination is conducted in large reverberatory furnaces, upon quantities of about 3 tons at a time; the heat is moderate, so as to avoid fusing the mass, which is spread evenly over the floor of the furnace, and stirred at intervals of 2 hours: this roasting is continued for 12 hours, at the end of which time the mass is converted into a black powder con-

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\* The apparent complication of the process arises from one of its great practical merits—viz., from the circumstance that it admits of being modified to suit almost every variety of ore, and these modifications necessarily tend to increase its complexity. Le Play enumerates six principal varieties of ores as being wrought by this method.—1. Pyritous ores, containing from 3 to 15 per cent. of copper. 2. Richer ores of the same kind, yielding from 15 to 25 per cent. of copper. 3. Siliceous oxides of copper, yielding from 12 to 20 per cent. of metal. 4. Oxides and carbonates with subsulphide of copper, in a siliceous matrix. 5. Very pure siliceous sulphides of copper and iron, yielding from 10 to 15 per cent. of copper; and 6. Pure sulphides and oxides of copper containing from 60 to 80 per cent. of the metal.

taining cupreous sulphide, oxide and undecomposed sulphide of iron, and earthy impurities. Oxygen has a stronger attraction for iron than for copper, but the attraction of sulphur for copper is greater than for iron; and the effect of the roasting is seen in the production of ferric oxide and sulphurous anhydride, whilst the cupreous sulphide remains unacted upon. During this and the subsequent processes, abundant white deleterious fumes are given off; containing arsenious, sulphurous, sulphuric, and hydrofluoric acids, and a certain portion of metallic arsenic. These fumes hang like a dense canopy over the smelting works and their vicinity: the cloud of *copper smoke*, as it is called, may be discerned at the distance of many miles.

The *calcining furnace* employed in Wales is shown in section in fig. 361, and a plan of the hearth is exhibited in fig. 362. A is

FIG. 361.

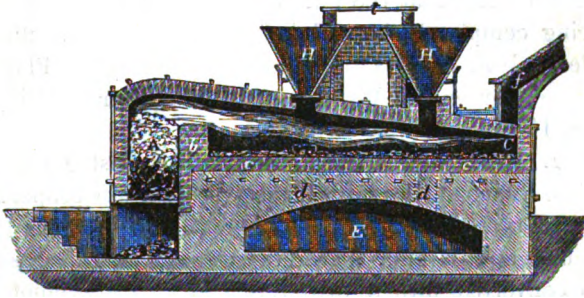
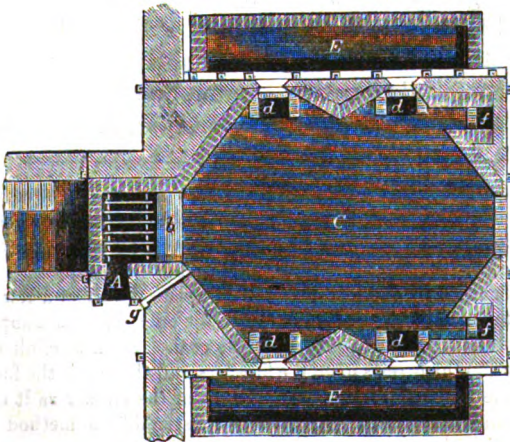


FIG. 362.



the fireplace: *b*, the bridge; *c c*, the hearth or roasting bed; *d, d*, are apertures in the floor, through which, by withdrawing an iron

slide, the charge can be allowed to pass into the *cub*, or vault, *e*, when the roasting is complete; *f, f*, are the flues; *g* is an opening for the admission of air to the hearth; *h, h*, are the hoppers for charging the furnace, and *t*, a platform over which the barrows of ore are conveyed to the hoppers.

The fuel used in roasting the ore is chiefly anthracite, a coal which, under ordinary management, yields no flame. Flame, however, is absolutely necessary to the proper roasting of the copper ore: experience has taught the copper smelter to obtain this desideratum by limiting the supply of air to the fuel in the fire-grate, thus causing the carbonic anhydride which is formed at the lower part of the fire to be converted into carbonic oxide. By a nice adjustment of the supply of air through *g*, the other apertures of the furnace being closed, the carbonic oxide is gradually burned as it plays over the ore upon the hearth, *c c*; the maximum of heat is thus obtained at the minimum cost of fuel, the carbonic oxide being completely burned before it reaches the flue. An admirable analysis of this operation is given by Le Play in his elaborate memoir on the Welsh method of copper smelting (*Ann. des Mines*, IV. xiii. 128).\*

(870) 2. *Melting for Coarse Metal*.—The roasted ore is now subjected to fusion in the *ore furnace* with certain proportions of slag, the produce of a subsequent operation, of siliceous ore free from sulphur, and of fluor-spar if necessary: by this means the charge is converted into a fusible slag, consisting chiefly of a ferrous silicate, and into sulphides of copper and iron, which sink through the slag, and form what is termed a *matt*. This fusion occupies about 5 hours, each charge containing about  $1\frac{1}{2}$  ton of roasted ore. The *matt* thus procured contains about 33 per cent. of copper: it is run off while liquid into water, by which it is granulated. The product goes by the name of *coarse metal*. The slag which

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\* The heat emitted during the combustion of anthracite is very intense, so that it causes a rapid oxidation of the fire-bars of the furnace. This fuel has also the inconvenience of splitting into small fragments, which choke the air-ways between the bars, if the heat be suddenly applied. The copper smelter overcomes these difficulties by employing a grate consisting only of a few bars, which do not come into contact with the fuel itself, but only serve as a support for the clinker produced during the combustion of the coal. A bed of clinkers, 12 or 16 inches (30 or 40<sup>cm.</sup>) thick, rests upon the fire-bars, and above this the fuel is burned: from time to time the fireman removes portions of the clinker as it accumulates.

Mr. Vivian has lately tried with success Gerstenhöfer's method of roasting these ores, in which they are supplied in a crushed state continuously to a furnace of special construction. The sulphur of the ore itself, after the furnace is lighted, maintains the necessary temperature for continuing the combustion, whilst the sulphurous acid is conducted into leaden chambers and converted into sulphuric acid.

floats above the matt is raked out of the furnace at a separate aperture. It ought to contain no appreciable quantity of copper.

3. *Calcination of the Coarse Metal.*—The granulated metal is again roasted for 24 hours, during which operation a large proportion of the sulphide of iron is converted into oxide.

4. *Melting for Fine Metal.*—A second fusion is performed upon this calcined matt with the addition of a portion of copper ore known to be rich in cupric oxide and in silica, and to contain but little iron pyrites. By this means the iron is removed in the form of a fresh slag of silicate of iron, and the oxygen contained in the freshly added cupric oxide completes the oxidation of any portion of iron pyrites still remaining; the oxide of copper and the whole of the sulphide of this metal being reduced to the state of cupreous sulphide ( $\text{Cu}_2\text{S}$ ) or *fine metal*. The slags from this process, and all the subsequent ones, are preserved. This matt contains about 80 per cent. of copper. It is cast into pigs. If a very pure metal be required, the roasting is carried a little further; a portion of the metal is thus reduced: this portion contains the greater part of the foreign metals, which give up their sulphur more readily than the copper; the reduced metal, from its greater density, sinks to the bottom; the upper parts of the pigs are subsequently detached from the lower portions, and the metal extracted from the upper portions of the ingots is known in the market as *best selected copper*.

5. *Roasting for Blistered Copper.*—The fine metal or cupreous sulphide is now to be freed from the sulphur, which has hitherto been useful by forming a fusible compound with the copper, thus facilitating its separation from the impurities by which it was accompanied. With this view the pigs of fine metal are next subjected, for several hours, upon the bed of a reverberatory, to a heat just short of that required to fuse them; the metal by this means becomes oxidized at the surface, and a part of the sulphur which it still retains is also oxidized; at last it is fused: a remarkable reaction then begins to take place. When cupric oxide and cupreous sulphide are heated together, they decompose each other; sulphurous anhydride and metallic copper are liberated;  $\text{Cu}_2\text{S} + 2\text{CuO} = \text{SO}_2 + 4\text{Cu}$ . It is not desirable that the temperature should be too strongly raised, as the cupric oxide would then combine with the silica still present in the mass, and would cease to exert its oxidizing influence. After the charge has become liquid, the temperature of the furnace is allowed to fall; the melted mass solidifies upon its surface, and an appearance of violent ebullition is produced from the formation of sulphurous

anhydride and its efforts to escape from the tenacious mixture : when this ceases, the desulphuration is complete. The heat is now rendered very intense, the copper melts and sinks to the bottom, and separates completely from the slag, which consists chiefly of cupreous silicate ; the reduced metal is then run off into sand moulds. The ingots thus obtained, being full of bubbles, are termed *pimple* or *blistered copper*.

(871) 6. *Refining or Toughening*.—The blistered copper now undergoes the concluding operation of refining. From 7 to 8 tons, or about 8000 kilos., of the metal are placed in a reverberatory furnace and kept in a melted state for upwards of 20 hours, in order to oxidate the last traces of foreign metals : during this process a large quantity of cupreous oxide is formed ; part of this oxide is absorbed by the melted metal, and the copper, if examined at this stage, is found to be of a dull red colour, coarse grained and brittle. To reduce this oxide, the slags are skimmed off, and the surface is covered with a few shovelfuls of anthracite or of charcoal ; the metal is then subjected to the process of *poling*, in which the trunk of a young tree is thrust into the molten metal. The inflammable gases disengaged from the green wood as it chars, produce a powerful agitation of the whole mass, and in about 20 minutes the poling is finished. The reducing influence of the combustible gases has in the mean time been brought to bear upon every portion of the melted metal. In this way the oxide diffused through the mass is deprived of oxygen. If the poling be carried too far, the copper again becomes brittle, and is said to be *overpoled*. This defect may be remedied by exposing the surface of the melted metal to a current of air. If too little poling be used, the metal is still brittle, and it is then said to be *underpoled*. The progress of the poling, therefore, requires careful watching : the refiner tests the metal from time to time by dipping a small test-ladle into the melted mass ; a sample of copper is thus removed, and cooled suddenly by immersion in water : the grain of the copper is judged of by cutting the hammered button partially through with a chisel or shears, and then bending it by placing it in a vice. If properly refined, the broken surface will display a fibrous structure with a beautiful silky lustre. If underpoled, the fracture will be granular, with a number of red points. If overpoled, the fibres become coarser, and the fracture has a strong metallic lustre, but the silky appearance is wanting. When, upon testing, the copper appears to be fine grained, fibrous, and silky, of good colour, and malleable, it is either ladled out and cast into ingots, or it is cooled suddenly at the surface, by allowing water to run upon it ; in the latter

case *rose copper* is produced, and successive films are made and removed till all the metal is consumed. There appears to be no doubt that the brittleness of underpoled copper is due to the presence of red oxide of copper in the metal, and Mr. Vivian has suggested that overpoled copper may be defective from the presence of a little carbon. Percy, however, was unsuccessful in the attempt to discover carbon in overpoled specimens. An interesting paper by Abel on the non-metallic impurities of refined copper will be found in the *Journ. Chem. Soc.* 1864, p. 164.

The slags from the various operations are carefully remelted, and the copper which is extracted from them is termed *black copper*; it is run into pigs, which are subsequently refined.

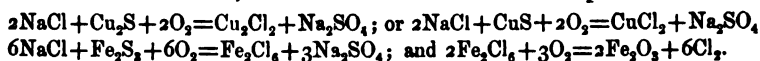
The presence of a small quantity of tin in the refined copper is considered to be advantageous, as the toughness and tenacity of the metal are thereby increased. Antimony is singularly injurious; so small a quantity as 1 part in 3600, or 10 ounces in the ton, renders copper unfit for making brass that is required for rolling; and minute traces of nickel and of bismuth are also said greatly to injure the tenacity of the metal.

(872) *Kernel roasting*.—When cupriferous iron pyrites, containing from 2 to 3 per cent. of copper, is broken into lumps of about the size of the fist, and subjected to a very gradual roasting, a large portion of the copper becomes concentrated in the middle of the lump, and a nucleus of sulphide of copper and iron is formed. This nucleus, or *kernel*, is surrounded by a more or less porous shell, composed mainly of ferric oxide, which may be detached from the nucleus by a blow. Upon these observations a method of roasting copper ore has been founded, to which the name of *kernel roasting* has been given. This roasting is conducted in the Venetian Alps, at Agordo, in kilns, and at Mülbach in enormous heaps in the open air. These heaps are in the form of a truncated square pyramid, the base of which is 9 or 10 metres, or about 30 feet square (406). The roasting is a very slow operation, requiring from 5 to 6 months for its completion. Spring and autumn are the most favourable seasons in which to commence it. Sulphur distils off to the extent of 0·2 (P) per cent. of the ore; the kernels constitute from 13 to 14 per cent. of the roasted mass, and they contain about 5 per cent. of metallic copper. The cause of this concentration of copper in the interior of the mass is entirely unexplained. The shells, which retain a small proportion of cupric sulphate, are washed to extract this as far as practicable, and the roasted ore is then subjected to processes not essentially differing from those already described. (Percy, *Metallurgy*, i. 439.)

In many copper mines the water which is pumped up is impregnated with cupric sulphate derived from the oxidation of the sulphide by exposure to the air: the copper is easily separated in the metallic form, by collecting the water in tanks containing scrap-iron: the iron unites with the oxygen and the acid, whilst the copper is set at liberty:  $\text{CuSO}_4 + \text{Fe} = \text{FeSO}_4 + \text{Cu}$ .

When the ore consists of the oxides and carbonates of copper, it is easily reduced to the metallic state by simple fusion with coke or charcoal, ferric oxide and lime being added in quantity sufficient to form a fusible slag with the silica which usually accompanies these ores; the copper is rendered tough by a process analogous to that of poling.

Mr. Henderson has recently introduced a process by which a good deal of copper is now extracted from a pyrites poor in copper. This pyrites, after it has been burned for the sake of its sulphur in the manufacture of oil of vitriol, furnishes a mass consisting chiefly of oxide of iron mixed with about 3 per cent. of copper, and from 6 to 8 per cent. of sulphur, with small quantities of arsenic, and sometimes of zinc and bismuth; the proportion of sulphur must be about 3 parts for every 2 parts of metal to be removed. It is ground to a fine powder after admixture with about 15 per cent. of salt, or about twice as much salt as of metal to be extracted. The mixture is then roasted for some hours at a low red heat. Copious fumes of hydrochloric acid, and free chlorine, mixed with chlorides of iron, arsenic, and other volatile metals are evolved whilst the greater part of the copper is converted into chloride, and the sodic chloride into sodic sulphate:



The roasted mass is lixiviated first with water, and then with weak acid, and finally is washed with water. The oxide of iron which is left is used for lining puddling furnaces. The liquors which contain the copper in solution are treated with scrap iron, and the copper which is precipitated is collected and refined by poling in the usual way.

The copper of commerce is often very nearly pure. It contains minute quantities of arsenicum, of iron, of lead, and sometimes of tin and silver. Abel has detected traces of selenium in some specimens, and of sulphur in others. Copper may be readily obtained in a state of perfect purity, by decomposing a solution of pure cupric sulphate by means of the voltaic battery: it is then deposited in coherent plates upon the negative electrode.

(873) *Properties.*—Copper is one of the metals which has been longest known to man: before the art of working iron was understood, it was in extensive use, either alone or alloyed with tin, for many of the purposes to which iron is now applied. It is of a well known red colour, and has a peculiar, disagreeable odour and taste when moistened and rubbed. It is rather a hard metal, very tenacious, ductile, and malleable; after it had been melted beneath a layer of common salt, to exclude atmospheric air, pure copper was found by Scheerer and Marchand to have a sp. gr. of 8.921: the density was increased by hammering, and when drawn into fine wire it was obtained as high as 8.952: Daniell estimated its fusing-point at  $1996^\circ$  ( $1091^\circ$  C.). When heated to a temperature approaching its melting-point it becomes so brittle that it may be reduced to powder, and an ingot may be broken by a blow from a hammer. If exposed to a very intense heat, copper is capable of volatilization, but it is usually considered to be fixed in the fire. By slow voltaic action it may be obtained crystallized in cubes and octohedra, and is sometimes found native in these forms. It ranks amongst the best conductors of heat and electricity. If heated to redness in the open air, copper com-

bines with oxygen rapidly, a layer of oxide is formed upon the surface, and as the oxide contracts more slowly than the metal beneath, it scales off if suddenly cooled, leaving a bright, clean, metallic surface. Copper is not oxidized when heated to redness in a current of steam. Exposure to a moist air at ordinary temperatures has no effect upon copper; neither has pure water; but in sea water, or in solutions of the chlorides, it is gradually corroded, with the formation of cupric oxychloride. Finely divided copper becomes ignited when touched with a glowing coal, and burns like tinder, being converted into the black oxide. Chlorine attacks the metal, which when in the form of leaf takes fire in the gas spontaneously. Nitric acid oxidizes and dissolves the metal with rapidity. Oil of vitriol does not act upon it in the cold, but if heated with it, the acid is decomposed, sulphurous anhydride being evolved and cupric oxide formed, which reacts upon the excess of acid to form the sulphate. Hydrochloric acid with excess of air dissolves it: but if air be excluded, it has no such effect at ordinary temperatures; though if boiled upon the finely-divided metal, it dissolves it very slowly, and hydrogen is evolved (Odling). Copper also decomposes hydrochloric acid gas when heated in it to redness, cupreous chloride being formed and hydrogen separated. The fixed alkalies have little action on copper, but ammonia gradually dissolves the metal if the air has access to it, slow oxidation taking place. Before the oxyhydrogen blowpipe it burns with a green flame, and if introduced into a flame of gas or of alcohol it communicates to it a green colour.

*Uses.*—The applications of copper in the arts are very numerous. Independently of its use in coinage, vast quantities of it are annually consumed in the sheathing of ships\* and in the manufacture of boilers, and of various utensils for domestic purposes. It also forms the basis of a number of valuable alloys in extensive use: with zinc it furnishes the different varieties of brass; and with different proportions of tin, it forms bronze, bell-metal, gun-metal, and speculum metal (812); whilst its oxides and salts are largely employed as pigments, and yield articles of some importance in the materia medica.

A compound of copper and silicon containing 12 per cent. of the latter may be obtained by fusing together 3 parts of potassic silicofluoride, 1 part of sodium and 1 of copper turnings: it is hard, brittle, and white, like bismuth. Another

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\* Percy's experiments appear to show that the presence of a small quantity of phosphorus in the copper has some effect in protecting the metal from the corrosive action of sea water.



alloy may be obtained by prolonged heating of a mixture of sand, charcoal, and copper: when it contains 4·8 per cent. of silicon it is of a fine bronze colour. It is as fusible as bronze, very ductile, and yields a wire a little softer than iron, but quite as tenacious: it may be worked well at the lathe.

(874) *Brass*.—The combination of zinc with copper has a well-known yellow colour, the tint of which becomes paler in proportion as the quantity of zinc is increased. A curious observation upon this point was made by D. Forbes, who found that a brittle crystalline alloy of a silver-white colour may be formed, containing 53·49 per cent. of zinc, and consisting of 7 equivalents of copper, and 8 of zinc; but if the quantity of zinc were either increased or diminished, the alloy had the usual yellow colour of brass. The specific gravity of brass is greater than the mean of that of the metals which form it. Ordinary brass has a sp. gr. of 8·29; it contains about 64 per cent. of copper, being nearly  $\text{Cu}_2\text{Zn}$ . Brass which contains 25 per cent. of zinc melts at  $1750^\circ$  ( $954^\circ\text{C}$ .; Daniell), and a larger proportion of zinc increases its fusibility. By exposure to a long-sustained high temperature in closed vessels, the whole of the zinc may be expelled, and it is not possible to fuse the alloy without losing a portion of the zinc. The alloys of zinc and copper are malleable when cold, but are generally brittle when hot. An alloy largely used under the name of *Muntz metal*, or *yellow metal*, for the sheathing of ships, may be rolled whilst hot: it contains 2 equivalents of zinc to 3 of copper, or 60 per cent. of copper. The addition of about 2 per cent. of lead to brass improves its quality if it is to be used at the lathe; it diminishes its toughness, and prevents it from hanging to the tool and clogging the file; but if intended for wire, the presence of lead must be avoided. A very small proportion of tin, even if it does not amount to 1 part in 200, greatly increases the hardness of the alloy. The ordinary *hard solder* for brass is an alloy consisting of 2 parts of brass and 1 of zinc. Brass is usually made by melting granulated copper in crucibles with rather more than half its weight of zinc: formerly a mixture of calamine and charcoal was substituted wholly or partially for metallic zinc. At Swansea, the Muntz metal is prepared by melting the two metals in a reverberatory furnace, which enables a large quantity of the alloy to be prepared with rapidity: but the process is attended with a considerable waste of zinc.

Gedge's and Aiche's alloys consist of a mixture of copper, zinc, and iron, which can be forged, cast, rolled, or drawn into wire; 100 parts of the best description of Gedge's alloy contain—copper 60 parts, zinc 38·2, and iron 1·8 parts. It is very hard, and appears to be well adapted to the sheathing of ships. It acquires great stiffness and elasticity if worked cold, but may be softened by

annealing. Another alloy of a similar kind, termed *sterro-metal*, consists of copper 55.04, zinc 42.36, iron 1.77, and tin 0.83 parts.

(875) OXIDES OF COPPER.—There are two salifiable oxides of copper, both of which are found in the native state; viz., the red or cupreous oxide ( $\text{Cu}_2\text{O}$ ), and the black or cupric oxide ( $\text{CuO}$ ); this last is the basis of the ordinary salts of the metal. Rose has lately pointed out the existence of a still lower oxide, which he terms a *quadrantoxide* ( $\text{Cu}_4\text{O}, x \text{H}_2\text{O}$ ); it is only known as a green hydrate of extreme oxidability, obtained by digesting a cupric salt in closed vessels for 24 hours with an excess of stannous chloride dissolved in a large excess of caustic potash. Some indications have been obtained of the existence of a still higher oxide than  $\text{CuO}$ , probably  $\text{Cu}_2\text{O}_3$ .

*Cupreous oxide, Red oxide or Suboxide of copper* ( $\text{Cu}_2\text{O} = 143$ ); *Sp. Gr.* 5.75; *Comp. in 100 parts*, Cu, 88.8; O, 11.2.—This compound occurs native, crystallized either in the octohedron, or in some of its derived forms, or else in capillary crystals or in lamellar masses. There are various ways of obtaining this oxide artificially; one of the best consists in boiling the dibasic cupric acetate with sugar; the cupric oxide is thus deprived of half its oxygen, and the red oxide is deposited in small octohedra. Another method consists in digesting copper foil in a solution of a salt of copper such as the sulphate, mixed with a large excess of ammonia, and warming the mixture in a vessel completely excluded from the air, the liquid becomes decolorized, and deposits the suboxide as a reddish-yellow powder. It may also be procured by igniting 5 parts of powdered cupric oxide with 4 parts of copper filings, in a covered crucible. The red oxide fuses at a full red heat. By decomposing cupreous chloride with potassic hydrate it is obtained as an orange-yellow hydrate ( $4\text{Cu}_2\text{O}, \text{H}_2\text{O}$ ; Mitscherlich). In this condition it is readily attacked by acids.

A cupreous sulphate, carbonate, and acetate appear also to exist. The cupreous salts are unstable, and absorb oxygen readily. Some of its double salts are more stable; a *cupreo-potassic sulphite* ( $\text{Cu}_2\text{SO}_3, 2\text{K}_2\text{SO}_3$ ) may be obtained as a yellow insoluble precipitate, by mixing solutions of normal or of hydropotassic sulphite with cupric sulphate; in this case, the cupric salt is reduced to the state of cupreous salt by the sulphite.

Cupreous oxide is soluble to some extent in metallic copper, which it renders, in technical terms, *dry*, or brittle. Abel found as much as 4.6 of the cupreous oxide in a specimen of very dry copper which he examined.\*

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\* Abel has contrived a method of determining the amount of oxide in the metal, founded upon the fact that cupreous oxide decomposes neutral argentic nitrate, furnishing an insoluble basic cupric nitrate,  $\text{Cu}_2\text{O} + 2\text{AgNO}_3 = \text{Ag}_2\text{O} +$

The anhydrous suboxide is resolved by most of the stronger acids into a cupric salt, and into metallic copper. Nitric acid converts it into cupric nitrate: but hydrochloric acid changes it into cupreous chloride, which is soluble in the excess of the acid. Hydrated cupreous oxide is soluble in a solution of ammonia, forming with it a colourless liquid. This solution is an extremely delicate test of the presence of oxygen in a gaseous mixture; a mere trace of oxygen causes it to assume a blue tint from the formation of cupric oxide, which when dissolved in a solution of ammonia has an intense blue colour. An ammoniacal solution of cupreous chloride, when mixed with a solution of argentic nitrate containing a large excess of ammonia, immediately deposits reduced silver in a fine state of subdivision, whilst argentic chloride and cupric nitrate are held in solution in excess of ammonia;  $\text{Cu}_2\text{Cl}_2 + 4\text{AgNO}_3 = 2(\text{Cu}_2\text{NO}_3) + 2\text{AgCl} + \text{Ag}_2$ . The principal employment of cupreous oxide is in the manufacture of stained glass, to which it imparts a beautiful ruby or purple colour.

(876) *Cupric oxide, or Black oxide of copper* ( $\text{CuO} = 79.5$ ); *Sp. Gr.* 6.5; *Comp. in 100 parts*, Cu, 79.85; O, 20.15.—This oxide is a compound of considerable importance to the chemist. It is employed largely as a means of furnishing oxygen to organic substances in the regulated combustion by means of which their composition is determined. The best process for obtaining the cupric oxide consists in dissolving copper in pure nitric acid, and decomposing the resulting nitrate in an earthen crucible, by the application of a red heat: the water and the nitric acid are thus expelled, and the black oxide remains in a state of purity: the heat should be long continued, but not too violent; otherwise the oxide sinters together and concretes into hard masses, which are pulverized with difficulty. A very pure oxide is also fur-

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$\text{Cu}_2\text{NO}_3, \text{CuO}$ . This basic salt is soluble in dilute sulphuric acid;  $\text{Cu}_2\text{NO}_3, \text{CuO} + 2\text{H}_2\text{SO}_4 = 2\text{HNO}_3 + \text{H}_2\text{O} + 2\text{CuSO}_4$ . The plan consists in digesting 500 or 600 grains (30 or 40 grammes) of the copper for trial in a solution of 400 grains (25 grammes) of neutral argentic nitrate in the cold, for three or four hours. The undissolved portion of copper is removed, washed into the solution of silver, dried, and weighed. The mixture of precipitated silver and insoluble basic cupric nitrate is separated by decantation from the solution, then washed, and digested for half-an-hour with a known quantity of standard sulphuric acid, being frequently agitated with it. It is filtered, and the washings neutralized by sodic carbonate. The proportion of acid neutralized by the basic cupric nitrate furnishes the means of estimating the quantity of cupreous oxide, 80 parts of  $\text{SO}_3$  being equivalent to 16 parts of oxygen in the sample, or to 143 of cupreous oxide.

nished by the decomposition of the carbonate by heat; or still more simply by heating a plate of copper to redness in a brisk current of air, and suddenly quenching it in water, in which case the oxide separates in black scales, the inner layer of which often contains a little red oxide. It may be obtained as a hydrate of a light blue colour ( $\text{CuO}, \text{H}_2\text{O}$ ), from any of its salts, by the addition of a slight excess of caustic potash, washing quickly with cold water, and drying at ordinary temperatures: when boiled with water the oxide becomes black and anhydrous. This hydrate is soluble in an excess of a solution of ammonia, forming a liquid with a splendid blue colour: if slips of metallic copper be introduced into a bottle which is filled with this liquid, and closed so as completely to exclude the air, a portion of the metal equal to that already in solution is dissolved, the metal deriving oxygen from the oxide already in solution, both portions being thus reduced to the state of cupreous oxide;  $\text{Cu} + \text{CuO} = \text{Cu}_2\text{O}$ ; the colour gradually disappears, since cupreous oxide produces a colourless solution with ammonia; but the moment that air is admitted, the blue colour is reproduced. Cupric oxide is soluble in oils and fats, so that greasy matters boiled in a copper saucepan which is not kept bright are liable to become impregnated with the metal. Cupric oxide combines with glass, and gives it a beautiful green colour. The oxide is hygroscopic, particularly if in a finely divided state, and it absorbs water rapidly from the air. Its oxygen cannot be expelled from it by mere exposure to heat, but if the oxide be plunged into an atmosphere of hydrogen while warm, it is decomposed with evolution of light and heat, while water is formed. Cupric oxide is soluble in most of the acids, and combines with them to form salts which have a green or a blue colour. When fused with potassic or with sodic hydrate, cupric oxide combines with the alkali, forming a greenish blue mass, which is decomposed by the addition of water.

Thénard obtained a combination of peroxide of hydrogen with cupric oxide; it was of a yellowish-brown colour, and when moist quickly underwent decomposition at ordinary temperatures.

(877) CUPREOUS HYDRIDE ( $\text{Cu}_2\text{H}_2$ ).—This substance was obtained by Wurtz, as a brown hydrate, when hypophosphorous acid was mixed with a solution of cupric sulphate, and heated to nearly  $140^\circ$  ( $60^\circ \text{C.}$ ). It is very unstable: when dry it is suddenly resolved at  $158^\circ$  ( $70^\circ \text{C.}$ ), into hydrogen gas and finely-divided metallic copper. It takes fire spontaneously in gaseous chlorine. Hydrochloric acid forms with it cupreous chloride, attended with a brisk disengagement of hydrogen. This disengagement of hydrogen gas from the acid as well as from the hydride is remarkable; Brodie explains it by supposing that the hydrogen of the hydride and that in the acid are in opposite electrical or polar conditions, in consequence of which they unite at the moment of liberation and form *hydride of hydrogen*, or hydrogen gas; thus,  $\text{Cu}_2\text{H}_2 + 2\text{HCl} = \text{Cu}_2\text{Cl}_2 + 2\text{H}_2$ .

(878) *Tricupric nitride* ( $\text{Cu}_3\text{N}$ ) is obtained by transmitting a current of dry ammoniacal gas over finely powdered cupric oxide heated to  $482^\circ$  ( $250^\circ \text{C.}$ ); water and nitrogen gas are evolved, and the nitride is left as a dark-green powder, which when heated to about  $590^\circ$  ( $310^\circ \text{C.}$ ) explodes feebly, emitting a red light; strong acids decompose it with evolution of nitrogen gas.

(879) **SULPHIDES OF COPPER.**—These are three in number:  $\text{Cu}_2\text{S}$ ;  $\text{CuS}$ ; and  $\text{CuS}_2$ .

*Cupreous sulphide*, or *Subsulphide of copper* ( $\text{Cu}_2\text{S}=159$ ; *sp. gr.* 5.735—5.977), is a soft mineral of a dark grey colour, occasionally found native in masses, but more often in six-sided prisms. It is easily fused by heat in closed vessels; nitric acid and aqua regia decompose it readily, but hydrochloric acid does not dissolve it. It may be formed by melting together 3 parts of sulphur and 8 of copper; vivid incandescence occurs at the moment of combination. It forms the *fine metal* of the copper smelter.

*Cupric sulphide*, or *Sulphide of copper* ( $\text{CuS}=95.5$ ), may be procured by the direct union of its constituents; it is also occasionally found native (*sp. gr.* 3.85) in flexible plates of a blue colour. It may likewise be obtained in the form of a dark-brown hydrate, by decomposing any of the salts of copper by a stream of sulphuretted hydrogen; this hydrate is quickly oxidized by exposure to the air, becoming converted into cupric sulphate, and it is dissolved easily by nitric acid and by aqua regia. Cupric sulphide is insoluble in a solution of dipotassic sulphide, but it is slightly soluble in one of diammonic disulphide,  $(\text{H}_4\text{N})_2\text{S}_2$ .

The *copper pyrites* (*sp. gr.* 4.3) or ordinary ore of copper, consists of a double sulphide of copper and iron  $\text{CuFeS}_2$ . It is of a yellow colour, and has a brassy lustre: it is sometimes found crystallized in tetrahedra, but it usually occurs in amorphous masses, with a conchoidal granular fracture, and is less hard than iron pyrites. The variety called variegated or *peacock ore* contains a larger proportion of sulphide of copper. These compounds are rapidly oxidized and dissolved by nitric acid or by aqua regia, but not by hydrochloric acid.

All the sulphides of copper are decomposed by roasting them in air; if the temperature be high, sulphurous anhydride escapes, and cupric oxide remains behind; at a lower temperature, cupric sulphate is formed.

Cupric sulphide forms likewise a natural combination with sulphides of lead, silver, antimony, and arsenicum, constituting grey copper ore, or *fahlerz*: this mineral is essentially a tetrabasic sulphantimonite and sulpharsenite of copper and iron; it varies considerably in the relative proportions of its constituents, and often contains zinc, lead, silver, and mercury. It crystallizes in forms derived from the regular tetrahedron, and in composition it corresponds to the

general formula ( $4MS, R_2S_3, 4M_2S, R_2S_3$ ), in which M represents the electro-positive metals,  $M_2S$  being usually cupreous or argentic sulphide: whilst R indicates the electro-negative metals arsenic or antimony. The principal varieties of the ore are:—1. *Tennantite* ( $FeS_3, 3CuS, As_2S_3, 4Cu_2S, As_2S_3$ ; *sp. gr.* 4.375), a ferrous and cupreous sulpharsenite, of a leaden-grey colour; the copper in this ore amounts to about 48 per cent. 2. *Light-grey copper ore* (*sp. gr.* 4.5 to 4.7), a mixture of sulpharsenite and sulphantimonite of zinc, iron, copper, and silver: colour, steel-grey. 3. *Dark-grey copper ore* (*sp. gr.* 4.7 to 4.9) contains little or no arsenic; it is of an iron-black colour. This variety and the one preceding it contain from 35 to 40 per cent. of copper. 4. *Silver fahlerz* (*sp. gr.* about 5.0), is a dark-grey copper ore, rich in silver. The silver varies in this ore from 13 to 30 per cent., and the copper from 14 to 25 per cent.

*Cupric pentasulphide* ( $CuS_5$ ) was obtained by Berzelius in the form of a blackish-brown precipitate, by decomposing a cupric salt with a pentasulphide of one of the alkali-metals. It undergoes no change by washing when exposed to the air, but is completely soluble in a solution of potassic carbonate.

A native *selenide of copper* is found in combination with selenide of silver. It occurs in masses of a leaden-grey colour, and is very rare, having hitherto been found only in Sweden: selenide of copper may be formed artificially by precipitating the cupric sulphate by seleniuretted hydrogen.

(880) *Phosphide of copper* ( $Cu_3P_2$ ?).—This compound is easily obtained by boiling phosphorus in a solution of cupric sulphate; the liquid speedily becomes decolorized, and a black phosphide of copper, with a semi-metallic lustre, is formed. It is not soluble in hydrochloric acid, but if thrown into a solution of potassic cyanide is decomposed rapidly without the application of heat, bubbles of self-lighting phosphuretted hydrogen being disengaged. Abel prepares phosphide of copper by transmitting the vapour of phosphorus over finely divided copper heated in a tube; he finds that this phosphide when mixed with potassic chlorate and gunpowder furnishes a powder of sufficient conducting power for electricity, and at the same time possessed of the requisite inflammability to enable it to be employed with great advantage as a detonating fuse for firing ordnance by magneto-electric currents.

(881) **CHLORIDES OF COPPER.**—Copper forms two chlorides,  $Cu_2Cl_2$ , and  $CuCl_2$ .

*Cupreous chloride*, or *Subchloride of copper* ( $Cu_2Cl_2 = 198$ ; *sp. gr.* 3.376) is obtained by distilling copper filings with twice their weight of corrosive sublimate; or by dissolving 4 parts of finely divided copper and 5 of the black oxide in hydrochloric acid; or by boiling cupric chloride with sugar; or by digesting cupric chloride in closed vessels with metallic copper: the last is a slow process, but part of the cupreous chloride is then deposited in transparent tetrahedra. It may also be obtained by heating dry cupric chloride in a current of dry ammonia until the whole is converted into a yellowish liquid, which solidifies on cooling to a white mass, with crystalline fracture, consisting of pure cupreous chloride. (Millon and Commaille, *Ann. de Chimie*, IV. iii. 285). Cupreous chloride is a white compound, which fuses easily into a yellowish mass; and darkens by exposure to light when moist. It is insoluble in water, but soluble to some extent in strong

hydrochloric acid, with which it forms a pale-brown solution, which deposits most of the subchloride on dilution. The solution of cupreous chloride in hydrochloric acid absorbs carbonic oxide gas with facility: a compound crystallizing in pearly scales ( $4\text{Cu}_2\text{Cl}_2 \cdot 3\text{CO}_2 \cdot 7\text{H}_2\text{O}$ ?; Berthelot) may thus be obtained; it is insoluble in water, which however decomposes it, setting cupreous chloride at liberty: it is also quickly decomposed by exposure to the air. Cupreous chloride is soluble in a boiling solution of potassic chloride; and if the liquid be allowed to cool excluded from the air, octohedral crystals, composed of  $(4\text{KCl}, \text{Cu}_2\text{Cl}_2)$  are deposited. When the solution in hydrochloric acid is exposed to the air, it absorbs oxygen rapidly, and a pale bluish-green insoluble cupric oxychloride ( $\text{CuCl}_2 \cdot 3\text{CuO} \cdot 4\text{H}_2\text{O}$ ) is deposited. This oxychloride is used in the arts as a pigment, under the name of *Brunswick green*. It is best procured by exposing copper clippings to the action of hydrochloric acid, or to a solution of sal ammoniac in the open air. It occurs native in the form of a green sand (sp. gr. 4.4), composed of small rhombic prisms, which is found at Atacama in Peru; it has hence been called *atacamite*. Sometimes it is also found massive. Other oxychlorides of copper of less importance may also be formed.

When finely divided copper is boiled in a solution of sal ammoniac, ammoniacal gas is expelled, and a salt is formed which is gradually deposited in white rhombic dodecahedra,  $(\text{H}_5\text{CuN}_2)'\text{Cu}'\text{Cl}_2$ : it may be regarded as cupreous chloride in which the second atom of copper has been displaced by *cupric diammonium*  $(\text{H}_5\text{Cu}'\text{N}_2)'$ . A solution of this salt, when exposed to the air, deposits blue crystals consisting of  $[(\text{H}_5\text{CuN}_2)'\text{Cu}'\text{Cl}_2, (\text{H}_5\text{CuN}_2)''\text{Cl}_2, \text{H}_2\text{O}]$ , and the mother-liquor on further exposure yields cubic crystals of the salt  $(\text{H}_5\text{CuN}_2\text{Cl}_2, 2\text{H}_4\text{NCl})$ .

(882) *Chloride of copper, or Cupric chloride* ( $\text{CuCl}_2 = 134.5$ ; sp. gr. 3.054) may be obtained by the spontaneous combustion of copper in chlorine, but it is more advantageously prepared by dissolving cupric oxide or carbonate in hydrochloric acid, when on evaporation it crystallizes in green needles, with the formula  $(\text{CuCl}_2 \cdot 2\text{H}_2\text{O})$  of sp. gr. 2.534. A concentrated solution of cupric chloride is of a green colour, but it becomes blue on dilution, and when the salt is anhydrous it is liver-coloured. When heated it fuses, and at a red heat half its chlorine is expelled, and cupreous chloride remains. It forms double chlorides with the potassic and ammonic chlorides. Cupric chloride is deliquescent, and very soluble in alcohol. This solution burns with a splendid green flame, the spectrum of which is shown in Fig. 81, No. 5; Part I. p. 172).

A double chloride of copper and ammonium ( $2\text{H}_4\text{NCl}, \text{CuCl}_2, 2\text{H}_2\text{O}$ ) is ob-

tained in blue square-based octohedra, by mixing hot concentrated solutions of the two salts in the proportion of 2 atoms of sal ammoniac and 1 of cupric chloride. Another double chloride ( $\text{H}_4\text{NCl}, \text{CuCl}_2, 2\text{H}_2\text{O}$ ) is obtained in fine, bluish-green crystals, by evaporating a solution of 1 atom of each salt.

Anhydrous cupric chloride absorbs ammonia rapidly, and forms a blue powder ( $\text{CuCl}_2, 6\text{H}_2\text{N}$ ; Rose), which by a heat of  $302^\circ$  ( $150^\circ \text{C.}$ ) loses 4 atoms of ammonia, and becomes green ( $\text{CuCl}_2, 2\text{H}_2\text{N}$ ; Kane). Graham and Kane regard this latter compound as ammoniac chloride in which the fourth atom of hydrogen has its place occupied by copper; hence Graham terms it *chloride of cuprammonium* ( $\text{H}_6\text{Cu}''\text{N}_2$ )' $\text{Cl}_2$ . If ammoniacal gas be transmitted through a hot concentrated solution of cupric chloride, till the precipitate at first formed is redissolved, the liquid on cooling deposits small dark-blue, square prisms and octohedra, [ $\text{H}_6\text{Cu}''\text{N}_2\text{Cl}_2, (\text{H}_4\text{N O})$ ].

It appears, therefore, that the following well-defined compounds may be obtained by the reaction of the chlorides of copper upon ammonia or muriate of ammonia:—

- (1.)  $\left. \begin{array}{c} (\text{H}_6\text{Cu}''\text{N}_2)' \\ \text{Cu}' \end{array} \right\} \text{Cl}_2$
- (2.)  $\left. \begin{array}{c} (\text{H}_6\text{Cu}''\text{N}_2)' \\ \text{Cu}' \end{array} \right\} \text{Cl}_2, (\text{H}_6\text{Cu}''\text{N}_2)''\text{Cl}_2, \text{H}_2\text{O}$
- (3.)  $(\text{H}_6\text{Cu}''\text{N}_2)''\text{Cl}_2$ , or  $\text{CuCl}_2, 2\text{H}_2\text{N}$
- (4.)  $(\text{H}_6\text{Cu}''\text{N}_2)''\text{Cl}_2, 4\text{H}_2\text{N}$ , or  $\text{CuCl}_2, 6\text{H}_2\text{N}$
- (5.)  $(\text{H}_6\text{Cu}''\text{N}_2)\text{Cl}_2, (\text{H}_4\text{N})_2\text{O}$
- (6.)  $(\text{H}_6\text{Cu}''\text{N}_2)''\text{Cl}_2, 2\text{H}_4\text{NCl}$
- (7.)  $2\text{H}_4\text{NCl}, \text{Cu}''\text{Cl}_2, 2\text{H}_2\text{O}$
- (8.)  $\text{H}_4\text{NCl}, \text{Cu}''\text{Cl}_2, 2\text{H}_2\text{O}$

(883) *Cupreous Bromide*, or *Sub-bromide of copper* ( $\text{Cu}_2\text{Br}_2$ ) is insoluble in water. *Cupric bromide* ( $\text{CuBr}_2$ ) is soluble.

*Cupreous iodide*, or *Subiodide of copper* ( $\text{Cu}_2\text{I}_2, \text{H}_2\text{O}$ ), is a white insoluble powder, which becomes yellow when heated. It is formed by pouring a mixture of 1 equivalent of ferrous sulphate, and 1 of cupric sulphate into a solution of any iodide; thus  $2\text{CuSO}_4 + 2\text{FeSO}_4 + 2\text{KI} = \text{K}_2\text{SO}_4 + \text{Fe}_2\text{SO}_4 + \text{Cu}_2\text{I}_2$ . Sodid sulphite may be substituted for the ferrous sulphate in this experiment. It has been proposed to employ such a mixture of the ferrous and cupric sulphates as a test for determining the quantity of iodine in kelp, in order to fix its commercial value. *Cupric iodide* ( $\text{CuI}_2$ ), if it exists, is very unstable.

**SULPHATES OF COPPER.**—Copper forms a normal sulphate, and several basic sulphates.

(884) *Cupric sulphate*, *Sulphate of copper*, or *Blue vitriol* ( $\text{CuSO}_4, 5\text{H}_2\text{O} = 159.5 + 90$ ); *Sp. Gr. anhydr.* 3.631; *cryst.*, 2.254; *Comp. in 100 parts cryst.*,  $\text{CuO}$ , 31.85;  $\text{SO}_3$ , 32.07;  $\text{H}_2\text{O}$ , 36.08.—This salt is manufactured on a large scale, by boiling copper in an iron pot with sulphuric acid, diluted with half its bulk of water: the acid is decomposed, and the copper is oxidized at its expense whilst the salt is precipitated. It may also be formed from an artificial sulphide of copper, by roasting it with free access of air, and lixiviating the roasted mass to dissolve the sulphate thus produced: the heat must be moderate, or else the sulphate will be decomposed during the roasting. If copper



pyrites be used instead of the artificial sulphide, the salt will contain a large quantity of ferrous sulphate, which cannot be separated by crystallization; for although cupric sulphate does not crystallize alone with more than  $5\text{H}_2\text{O}$ , yet when mixed with ferrous sulphate, it, like this salt, assumes  $7\text{H}_2\text{O}$ , and then is isomorphous with the ferrous salt. The only plan in such a case is to ignite the mixed sulphates feebly: the iron salt parts with its acid at a lower temperature than the copper salt, and by a second solution the iron is separated in the form of an insoluble oxide. Cupric sulphate is also obtained in considerable quantity as a secondary product in the refining of silver (947): the silver is precipitated from the solution of its sulphate in the metallic form, by plates of copper, and a pure cupric sulphate is thus furnished.

Large quantities of cupric sulphate are used in calico-printing, and it is the salt from which most of the pigments of copper are formed. It is soluble in four times its weight of water at  $59^\circ$  ( $15^\circ$  C.), and crystallizes in beautiful blue crystals of the doubly oblique rhombic form. The powdered crystals absorb hydrochloric acid gas rapidly with evolution of heat, and furnish a deliquescent mass. When cupric sulphate is heated to  $100^\circ$  C. it loses  $4\text{H}_2\text{O}$ , and by a temperature of  $392^\circ$  ( $200^\circ$  C.), the salt is rendered anhydrous; it then assumes the appearance of a white powder, which becomes blue on the addition of water. The act of combination with water is attended with a hissing noise, owing to the great rise of temperature which attends the action; a considerable evolution of heat also attends the combination of the compound  $\text{CuSO}_4\cdot\text{H}_2\text{O}$ , with water. Cupric sulphate is insoluble in alcohol. When heated to bright redness the elements of sulphuric anhydride are expelled, and cupric oxide is left.

Cupric sulphate forms double salts with the sulphates of potassium and ammonium; they are easily obtained by mixing solutions of their constituent salts in equivalent proportions, and allowing the mixture to crystallize. The potassium salt is composed of  $(\text{CuSO}_4\cdot\text{K}_2\text{SO}_4\cdot 6\text{H}_2\text{O})$ ; *sp. gr.* 2.244; the ammonium salt of  $[\text{CuSO}_4\cdot(\text{H}_4\text{N})_2\text{SO}_4\cdot 6\text{H}_2\text{O}]$ ; *sp. gr.* 1.891. According to Graham, a hot saturated solution of potassio-cupric sulphate deposits a remarkable basic double salt, the composition of which may be represented by the formula  $(\text{K}_2\text{SO}_4\cdot 3\text{CuSO}_4\cdot \text{CuO}\cdot 4\text{H}_2\text{O})$ .

*Basic Sulphates.*—If a solution of 1 atomic proportion of cupric sulphate is boiled with less than 1 atom of hydrated cupric oxide, a green insoluble *tribasic sulphate*  $[\text{CuSO}_4\cdot 2(\text{CuO}\cdot\text{H}_2\text{O})]$  is formed. *Brochantite* is a native basic sulphate of the metal, composed of  $[\text{CuSO}_4\cdot 3(\text{CuO}\cdot\text{H}_2\text{O})]$ ; and Denham Smith obtained another basic salt consisting of  $(\text{CuSO}_4\cdot 4\text{CuO}\cdot 6\text{H}_2\text{O})$ .

Anhydrous cupric sulphate absorbs dry ammoniacal gas; the compound consists of  $(\text{CuSO}_4\cdot 5\text{H}_3\text{N})$ ; (H. Rose). If ammonia be added in excess to a solution of cupric sulphate, the liquid on evaporation yields dark blue crystals  $(\text{CuSO}_4\cdot$

$4\text{H}_3\text{N}, \text{H}_2\text{O}$ ; Berzelius); the salt, when heated to  $302^\circ$  ( $150^\circ \text{C.}$ ), becomes green, losing two atoms of ammonia and one atom of water.

(885) *Cupric nitrate* ( $\text{Cu}_2\text{NO}_3, 6\text{H}_2\text{O}$ ) is easily made by dissolving copper in nitric acid: it forms a beautiful blue deliquescent salt, which crystallizes in rhomboidal prisms. At temperatures above  $15^\circ \text{C.}$  it crystallizes with  $3\text{H}_2\text{O}$  in deliquescent needles of sp. gr.  $2.047$ . It is very soluble in alcohol; by heat it is decomposed, first into a green *basic nitrate* [ $\text{Cu}_2\text{NO}_3, 3(\text{CuO}, \text{H}_2\text{O})$ ; Gerhardt], which is insoluble; and if the heat be increased, it is converted wholly into the black oxide, the whole of the nitric anhydride being expelled. It is this basic nitrate which is formed when cupric oxide is treated with monohydrated nitric acid, although the acid may be in considerable excess. If a few crystals of cupric nitrate are moistened and wrapped up in tinfoil they act violently upon the metal, and convert it rapidly into stannic oxide with emission of sparks.

Several basic cupric *phosphates* are found native in small quantities.

(886) **CARBONATES OF COPPER.**—All attempts to procure the neutral cupric carbonate have hitherto failed. A *hydrated oxycarbonate*, called *chessylite* [ $\text{CuO}, \text{H}_2\text{O}, 2\text{CuCO}_3$ ; sp. gr.  $3.8$ ], forms a beautiful blue mineral, which crystallizes in oblique rhombic prisms. But the most abundant of the carbonates of copper is the hydrated dibasic carbonate, or *malachite* ( $\text{CuO}, \text{H}_2\text{O}, \text{CuCO}_3$ ; sp. gr. from  $3.7$  to  $4.0$ ). It forms a very hard mineral of a silky lustre, and a beautiful green colour; it is susceptible of a high polish, by which its concentric and often beautifully veined structure is advantageously displayed. It is often employed for ornamental purposes. Malachite is occasionally found in oblique prisms. Both the blue and the green carbonate are abundant in the copper ore furnished from Australia. A green precipitate, sometimes used as a pigment, which has the same composition as malachite, and is known as *mineral green*, may be obtained by mixing hot solutions of cupric sulphate or nitrate and sodic carbonate. If the solutions be mixed cold, a pale blue voluminous precipitate is formed, which, according to Brunner, is the same compound, with an additional atom of water ( $\text{CuO}, 2\text{H}_2\text{O}, \text{CuCO}_3$ ). By boiling the precipitated carbonate, it becomes first green and then black, losing nearly all its water and carbonic acid. A double carbonate of potassium and copper ( $\text{K}_2\text{CO}_3, 4\text{CuCO}_3, \text{CuO}, 10\text{H}_2\text{O}$ ) may be obtained by digesting the green carbonate in a solution of hydropotassic carbonate: it is deposited in blue crystals by

spontaneous evaporation. Similar salts may be formed with sodium and ammonium.

(887) CHARACTERS OF THE SALTS OF COPPER.—1. *Salts of the suboxide, or Cupreous salts.*—Nearly all of them are insoluble in water, but soluble in hydrochloric acid; in this form they absorb oxygen rapidly, and are converted into salts of the black oxide. They are unimportant, and have been but little studied; one of their most remarkable properties is their power when in solution in hydrochloric acid of absorbing carbonic oxide, with which they form a crystalline compound.

2. *Salts of the black oxide, or Cupric salts.*—Most of these salts of copper have a green or a blue colour when hydrated, but they are white when anhydrous; they are almost all soluble. They have a strong, disagreeable metallic taste, and act as poisons to the animal frame, producing violent and irrepressible vomiting and purging, followed by exhaustion and death. They form an insoluble compound with albumin, which is nearly inert; raw whites of eggs should therefore be administered in cases of poisoning suspected to be occasioned by this metal. Milk or sugar mixed with iron filings, by reducing the cupric to cupreous salts, or to the metallic state, are also valuable adjuncts.

The cupric salts are easily recognized when in solution: though neutral in composition they reddens litmus. *Caustic potash and soda* give in their solutions a pale blue voluminous precipitate of hydrated basic salt; an excess of the alkali does not dissolve it, but converts it into a blue hydrated oxide, which becomes black and anhydrous when the liquid is boiled with it. If sugar or tartaric acid, or certain other organic substances be present, the blue precipitate is redissolved by an excess of the alkaline liquid, and forms a blue solution. *Ammonia* gives a similar blue precipitate; but an excess of the alkali redissolves it, forming a deep blue solution, which is very characteristic. *Potassic or sodic carbonate* gives a pale blue hydrated basic carbonate, which becomes gradually converted into the black oxide when boiled in the liquid with excess of the alkaline carbonate. *Ammonic sesquicarbonate* also gives a blue precipitate, but redissolves it if added in excess, forming an intensely blue solution. *Potassic ferrocyanide* yields a bulky brown precipitate, insoluble in hydrochloric acid, but soluble in ammonia, which leaves it unaltered on evaporation. *Sulphuretted hydrogen* gives even in acid solutions a brownish-black hydrated sulphide. The last two characters distinguish the salts of copper from those of nickel, which also form a blue solu-

tion with ammonia. Cupric sulphide is almost insoluble in ammonia, and in ammoniac hydrosulphide, but is dissolved by potassic cyanide. Another characteristic and very delicate test of the presence of copper is afforded by the action of a polished plate of *iron*, which, in a feebly acid solution, is speedily covered with a red deposit of metallic copper. *Zinc* precipitates copper in the form of a black powder, which assumes a metallic lustre under the burnisher. If a salt of copper be heated with sodic carbonate on charcoal *before the blowpipe* in the reducing flame, a bead of metallic copper may be obtained, and may be recognized by its colour and its malleability. Most copper salts when heated on platinum wire communicate an intense green colour to the oxidizing flame.

In cases in which the presence of copper is suspected in admixture with organic matters, as in the contents of the stomach, where it is supposed to have acted as a poison, the material must be reduced to dryness, and incinerated in an earthen crucible. The ash is then to be treated with nitric acid, and the liquid tested with ammonia, with potassic ferrocyanide, and with a steel needle. The copper-coloured deposit on the steel may be further identified by placing it in a narrow tube with a few drops of ammonia, which will become blue in the course of 24 hours if copper be present (Taylor).

The salts of copper have considerable tendency to form double compounds with other salts, and frequently basic salts of this metal may be procured with various acids: those with the sulphuric, nitric, carbonic, and acetic acids are the most important.

(888) *Estimation of Copper*.—This is generally effected in the form of the black oxide, 100 parts of which correspond to 79·85 of the metal. If the solution contain no metal precipitable by potassic hydrate, an excess of solution of potash is added, and the liquid is boiled; the precipitate is well washed with boiling water.

Pelouze (*Ann. de Chimie*, III. xvi. 426) has described a method of estimating the quantity of copper, by bringing it into solution with excess of ammonia, and ascertaining the quantity of a standard solution of disodic sulphide which is required to decolorize the liquid. The process is rapid, and admits of being applied in a large number of cases.

A still better method, according to E. O. Brown (*Q. J. Chem. Soc.* x. 65) consists in treating the solution of copper with one of potassic iodide; cupreous iodide ( $\text{Cu}_2\text{I}_2$ ) is thus formed, and iodine is set at liberty: the amount of the latter is determined by a standard solution of sodic hyposulphite: in order to effect the operation a weighed quantity of the ore is dissolved in nitric acid, boiled till red fumes cease to escape, and the nitrous acid is all expelled: it is then diluted with water, and sodic carbonate added until a slight permanent precipitate is formed. Acetic acid in excess is added, and afterwards an excess of potassic iodide and a few drops of a solution of starch. The quantity of iodine thus set free is then estimated by the number of divisions of a standard solution of sodic hyposulphite required to oxidize the iodine, a point which admits of most accurate determination by the disappearance of the blue tinge. The solution of hyposulphite is

graduated by dissolving 0.5 grm. of pure copper in nitric acid, and subjecting it to a series of operations exactly corresponding to those performed upon the ore, noting the number of divisions of the standard solution consumed in neutralizing the amount of iodine set free.

Copper may be readily separated from the metals of the first five groups, with the exception of cadmium, by the action of sulphuretted hydrogen. The precipitated cupric sulphide must be washed with water containing sulphuretted hydrogen in solution, in order to prevent its oxidation on the filter. The precipitate must be detached from the filter, redissolved in nitric acid (727), and the cupric oxide precipitated by means of caustic potash.

If cadmium be present, Stromeier directs that the precipitate of the mixed sulphides, obtained by transmitting sulphuretted hydrogen through the liquid, be redissolved by nitric acid, and precipitated by an excess of ammoniac sesquicarbonate, which, if left to stand for a few hours, dissolves the copper, but leaves the cadmium in the form of carbonate.

The separation of copper from bismuth may be effected by means of ammoniac sesquicarbonate, as directed for cadmium.

The other metals of the sixth group are separated by precipitating them with the copper as sulphides, and then digesting the mixed sulphides with a solution of potassic hydrosulphide (ammoniac hydrosulphide dissolves traces of copper); the cupric sulphide alone remains undissolved.

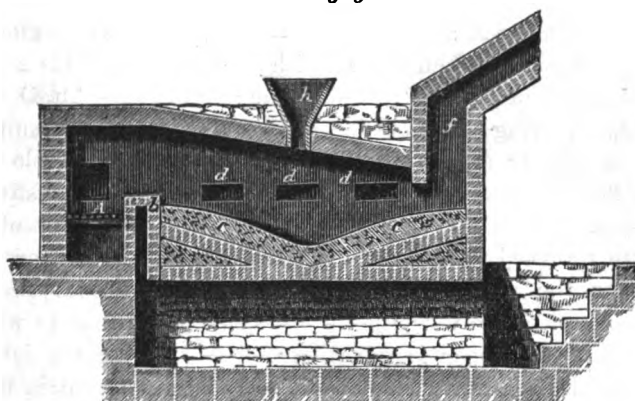
§ II. LEAD (Plumbum):  $Pb'' = 207$ . *Sp. Gr.* 11.36; *Fusing-pt.*  $617^{\circ}$  ( $325^{\circ}$  C.); *usually Dyad, as in*  $PbCl_2$ ; *sometimes Tetrad, as in*  $Pb(C_2H_5)_4$ .

(889) ALMOST all the lead of commerce is obtained from galena, the native plumbic sulphide. It occurs, mixed with quartz, blende, pyrites, baric sulphate, and fluor-spar, in veins traversing the primitive rocks, and particularly in the clay-slate in Cornwall, and mountain limestone in Cumberland. Small quantities of plumbic carbonate and phosphate are frequently met with, but they are unimportant as ores of the metal. Galena always contains a small proportion of argentic sulphide; when the mineral is found in bold, well-characterized cubes, it is usually nearly pure. The proportion of silver in galena is liable to considerable variation; a mineral yielding 120 ounces of silver to the ton, or 0.36 per cent., is considered to be extremely rich. England and Spain afford the principal supply of this metal, about 65,000 tons of lead being annually raised in England, which furnish on the average 560,000 ounces of silver.

(890) *Extraction*.—After the lead ore has been raised to the surface, it undergoes a careful mechanical preparation, conducted upon the principles already explained (529); and having been thus freed to a great extent from its earthy impurities, it is ready for smelting.

If the galena be tolerably free from siliceous gangue, this operation is sufficiently simple. About  $1\frac{1}{2}$  ton of the dressed ore is mixed with from a fortieth to a twentieth of its weight of lime, and is heated to dull redness in a reverberatory furnace, through which a strong current of air is passing. Fig. 363 exhibits a

FIG. 363.



section of the reducing furnace employed in Derbyshire. *A* is the fire-grate, *b* the bridge, *h* the hopper by which the charge is introduced; *c c*, the bed on which the ore is placed, sloping downwards towards a gutter in the centre, by which the melted metal is drawn off; *d, d, d*, are doors for working the charge and for admitting air, the draught of the furnace being completely under control by a damper placed in the flue *f*.

During the roasting a large quantity of the sulphur burns off as sulphurous anhydride, and a portion of plumbic oxide is formed: another portion of the plumbic sulphide is converted into sulphate, and much of the ore still remains undecomposed. In the course of the operation, the mass is frequently stirred, and care is taken not to allow the temperature to rise sufficiently high to fuse it. When it is considered that the roasting has been carried far enough, the materials on the bed of the furnace are thoroughly mixed together, the furnace doors are closed, and the heat is suddenly raised. The plumbic oxide and sulphate then react upon the undecomposed sulphide of the metal; a large quantity of sul-

phurous anhydride is evolved, whilst metallic lead runs copiously from the mass. The successive stages of this operation may be traced as follows :—

Two atoms of plumbic sulphide, by combining with 6 of oxygen, furnish 2 atoms of plumbic oxide and 2 of sulphurous anhydride, as is exhibited by the equation :  $2\text{PbS} + 3\text{O}_2 = 2\text{PbO} + 2\text{SO}_2$ . If 1 atom of galena unite with 4 atoms of oxygen, 1 atom of plumbic sulphate is formed :  $\text{PbS} + 2\text{O}_2 = \text{PbSO}_4$ . Both plumbic oxide and sulphate, when heated with fresh sulphide of lead, are decomposed, metallic lead and sulphurous anhydride being in each case the result of the reaction. Two atoms of plumbic oxide and 1 of galena furnish 3 of lead and 1 of sulphurous anhydride :  $2\text{PbO} + \text{PbS} = 3\text{Pb} + \text{SO}_2$ . One atom of plumbic sulphate, when heated with 1 of galena, yields 2 atoms of lead and 2 of sulphurous anhydride : thus  $\text{PbS} + \text{PbSO}_4 = 2\text{Pb} + 2\text{SO}_2$ . During the roasting a portion of plumbous sulphide,  $\text{Pb}_2\text{S}$ , is also produced. This substance forms a fusible matt, which flows from the furnace with the metallic lead, constituting a stratum which floats above the melted metal. This subsulphide is again returned to the furnace and roasted with fresh ore.

After the melted mass has been drawn off into cast-iron basins placed for its reception, a few spadefuls of lime to which a quantity of fluor-spar is sometimes added, are thrown into the furnace, with a view to act upon the scorixæ which remain behind in considerable quantity : the lime decomposes the fusible plumbic silicate, liberates plumbic oxide, and forms a less fusible calcic silicate, and the fluor-spar forms a fusible compound with the calcic or baric sulphate, if either of them is present. The scorixæ usually contain an excess of plumbic oxide and sulphate ; they are therefore mixed with coke or charcoal, and exposed to heat on the bed of the furnace, after the doors have been carefully closed : the plumbic oxide then becomes reduced by the carbon.

*Refining of Lead.*—Lead which contains antimony or tin is harder than the pure metal, and is subjected to a further operation, termed *improving*, in order to refine it. This consists simply in melting the lead, and heating it for a period, longer or shorter, as may be necessary, in a shallow cast-iron pan set in the bed of a reverberatory furnace ; the antimony and tin being more oxidizable than the lead, are thus removed in the pellicle of oxide which is continually being formed. From time to time the workman takes out a small sample of the metal to examine the appearance which it presents on cooling. As soon as it exhibits a peculiar flaky crystalline appearance on the surface,

the oxidation has been carried far enough ; the metal is then run off and cast into pigs.

(891) *Concentration of Silver in Lead by Pattinson's Process.*—

Silver may be profitably extracted from lead, even when the quantity does not exceed from three to four ounces of silver to the ton, by a process introduced by Mr. Pattinson, of Newcastle. This gentleman observed that if melted argentiferous lead be briskly stirred during slow cooling, a portion of the metal solidifies first, in the form of crystalline grains, which sink to the bottom of the still fluid portion. These crystals consist of lead nearly free from silver, the fusing-point of the argentiferous alloy occurring at a lower temperature than that of pure lead. This observation is turned to account in the following simple manner:—

Eight or nine cast-iron pots, each capable of containing about five tons of melted lead, are arranged in a row, set in brickwork, and each provided with a separate fireplace underneath. A quantity of lead is introduced into the middle pot, and melted ; the fire is then withdrawn, and the metal is briskly stirred by the workman whilst it cools : the crystals of lead subside as they form, and are removed at intervals by means of a large perforated iron ladle, and transferred to the next pot on the right hand. When about four-fifths of the metal have been thus removed in crystals, the concentrated argentiferous alloy is ladled out into the next pot on the left-hand side, and the empty pot is charged with a fresh portion of lead, which is subjected to a similar treatment. When the pot to the right and to the left has in this manner received a sufficient quantity either of poor or of argentiferous lead, it is subjected to a similar operation ; the concentrated argentiferous portion being passed off continually to the next pot on the left, whilst the crystalline or poorer portion is handed over to the next pot on the right-hand side. The last pot to the left thus at length becomes filled with lead which may contain 300 ounces of silver to the ton (0.9 per cent.) ; it is not found advantageous to concentrate it beyond this point : the lead which accumulates in the last pot on the right-hand side does not contain more than half an ounce of silver in the ton. This poor lead is much improved in quality by the operations which it has undergone, and is at once cast into pigs for the market.

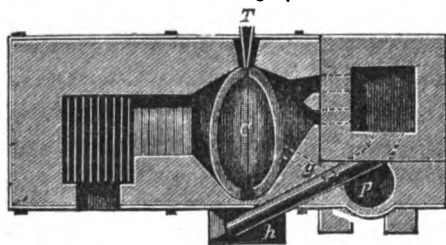
(892) *Extraction of Silver from Lead by Cupellation.*—The rich argentiferous lead is now subjected to *cupellation*. This process is founded upon the circumstance that lead, if exposed at a high temperature to a current of air, absorbs oxygen rapidly,



and is converted into a fusible oxide, while silver does not become oxidized, but is left behind in the metallic state. The litharge or plumbic oxide melts at a high temperature, and flows off the convex surface of the melted metal, and thus continually exposes a fresh surface of lead to the action of the air.

In England the cupellation is performed in a low-crowned reverberatory furnace, the hearth of which is moveable. The

FIG. 364.



hearth or *cupel* is shown in the plan of the furnace (fig. 364): it consists of a shallow oval basin, *c*, composed of a mixture of bone ash with fern or wood ashes; this mixture is slightly moistened, and beaten into an iron ring of about 4 feet in its long

diameter, and 2 feet in the shorter (1·2 by 0·6 metre): the cupel is introduced into the furnace from beneath, and is supported by bricks, so that it can be readily removed and renewed,—an operation which is generally required once a week. When dry, the fire is lighted cautiously, and the lead introduced; a continual blast of air from a tuyère, *t*, is made to play over the surface of the melted metal; litharge is formed abundantly, and runs off through a gutter, *g*, into an iron pot, *p*, placed beneath the furnace for its reception; in front is a hood, *h*, for carrying off the fumes of oxide of lead which would otherwise escape and injure the workmen. Fresh lead is added from time to time to supply the place of that which is oxidized; until at length a quantity of lead, originally amounting to about 5 tons, is reduced to between 2 and 3 cwt. This melted metal is withdrawn by making a hole through the bottom of the cupel; the aperture is afterwards closed with fresh bone ash, and another charge is proceeded with. When a quantity of rich lead sufficient to yield from 3000 to 5000 ounces of silver, or from 93 to 155 kilos. has thus been obtained, it is again placed in a cupel, and the last portions of lead are removed. It is found advantageous to effect this final purification of the concentrated silver-lead separately, because in the last stages of the operation the litharge carries a good deal of silver down with it: these portions of litharge, therefore, on being reduced, are again subjected to the desilvering process.

The litharge from the first fusion is either sold as such, or it

is reduced in a small reverberatory furnace with anthracite, or powdered coal. The porous cupels absorb a large quantity of litharge, and they likewise are passed through the furnace in order to extract the metal.

A very beautiful phenomenon, known as the *fulguration* of the metal, attends the removal of the last portions of lead from the silver. During the earlier stages of the process, the film of plumbic oxide, which is constantly being formed over the surface of the melted mass, is renewed as rapidly as it is removed; but when the lead has all been oxidized, the film of litharge upon the silver becomes thinner and thinner as it flows off; it then exhibits a succession of the beautiful iridescent tints of Newton's rings: and at length the film of oxide suddenly disappears, and reveals the brilliant surface of the metallic silver beneath.

In the Hartz the hearth of the cupellation furnace is fixed, and is made of brick, covered with marl, which is renewed after each operation, but the cover of the furnace is moveable. Karsten states that the advantage of this method is, that the litharge runs off more perfectly, and that there is less waste of silver from absorption into the cupel, and less expenditure of labour and fuel upon recovering the lead from the bottom of the furnace, which absorbs comparatively little litharge.

(893) In the North of England, the galena is smelted by a process somewhat different: the ore is first roasted, and then reduced in a small square blast furnace, or forge hearth,—dried peat being the fuel principally employed. This form of furnace is known as the *Scotch furnace*.

In some parts of the Hartz, where the ores are largely mixed with siliceous matters, the English method of smelting is not applicable, as the silica would combine with the oxide of lead, and form a fusible slag. It is found necessary in these cases to reduce the sulphide of lead by means of metallic iron, which is added in the form of granulated cast-iron, in the proportion of about 1 part of iron to 20 of pure galena. The fusion is performed in a small blast furnace, about 6 metres high and 0·9 m. across, or 20 feet high, and 3 feet across at the widest part.

These various furnace operations are attended by a continual disengagement of white fumes, which consist principally of plumbic oxide and sulphate, and are technically termed *froth of lead*; in this way nearly a seventh of the whole lead is volatilized. Independently of the waste thus occasioned, the fumes are highly deleterious; it is therefore of great importance to prevent as far as possible their diffusion through the air. It is stated that in the Hartz about  $\frac{1}{10}$  of the volatilized portion is arrested by causing the gases from the furnaces to pass through a succession of condensing chambers, before they finally escape into the air. At Allenheads, in Cumberland, a flue which ascends the side of a hill of three miles in length has been employed to conduct these fumes.

(894) *Properties*.—Lead is a bluish white metal, so soft that it may easily be made to take impressions: it leaves a streak upon paper, and may be cut with the nail. It may be laminated into tolerably thin sheets, as well as drawn into wire; but in both ductility and tenacity it is low in the scale. It fuses at 620° (327° C., Person; or 325° C., Rudberg), and may with some

difficulty be obtained in cubic or in octohedral crystals as it cools : the purer the lead the larger the crystals (Baker, quoted by Matthiessen). Lead contracts considerably at the moment of its solidification, and it is therefore not well adapted for castings. It appears to have the power, when melted, of dissolving a small quantity of plumbic oxide, by which the hardness of the metal is much increased ; but its softness may be restored by keeping it melted under charcoal for some time, with occasional agitation. As a conductor of heat and electricity, it is inferior to many of the metals.

At high temperatures, lead absorbs oxygen rapidly from the air ; it undergoes partial volatilization, and emits white fumes of oxide. It is not acted upon by sulphuric or hydrochloric acid at ordinary temperatures, and but slightly even when boiled with them ; but it is dissolved with extrication of nitric oxide, by nitric acid, especially when the acid is somewhat diluted. The vapours of acetic acid corrode it rapidly, and if carbonic acid be also present, convert it gradually into white lead. Green oak wood, from the quantity of acetic acid which it contains, should not be used in contact with lead for building purposes. The alkalis do not exercise any decided influence upon lead. Chlorine also slowly converts the metal into chloride, but the film of this compound, which is formed on the surface, protects the metal beneath. In the presence of moisture, lead is corroded when in contact with calcic sulphate ; hence in its application to architectural purposes, the contact of stucco or plaster with lead should be avoided.

The lead of commerce is often nearly pure. The purest specimens are the softest. Traces of tin, iron, copper, and silver, and sometimes of antimony and manganese, are the impurities which are most often observed. In order to obtain it perfectly pure, it should be reduced with black flux from the oxide left by igniting the pure nitrate or carbonate of the metal.

(895) *Combined Action of Air and Water on Lead.*—The surface of a piece of lead when freshly cut presents a high metallic lustre, but it soon tarnishes by exposure to air, owing to the formation of a thin, closely adhering film of oxide, which protects the metal from further change. Lead undergoes no alteration in a perfectly dry atmosphere, and even when sealed up in a vessel of pure water, which has been boiled for some time to expel the air, the metal will retain its brilliancy for an indefinite period ; but if it be exposed to the united action of air and *pure*

water, it is subject to a powerful corrosion. As the result of this exposure the lead becomes oxidated at the surface, and the water dissolves the oxide of lead; this solution absorbs carbonic acid, a film of hydrated basic carbonate of lead ( $\text{PbOH}_2\text{O}, \text{PbCO}_3$ ) is deposited in silky scales, and a fresh portion of oxide is formed and dissolved by the water; thus a rapid corrosion of the metal takes place. This action is modified very materially by the presence of various salts in the water, even though the quantity of these salts may not exceed 3 or 4 grains in the gallon (43 to 57 mgrms. per litre). The corrosion is much increased by the chlorides and nitrates. The presence of very minute quantities of the nitrites in water confers upon it a corrosive action on lead. Both nitrites and nitrates are often present in spring and river waters, owing to the decomposition of organic matter; and it is not improbable that the unexplained corrosive action of certain soft waters upon lead may be due to the presence of these salts, which might easily be overlooked in the course of the analysis (Medlock). Small quantities of ammonia also favour the solution of the metal. On the other hand, the corrosion is diminished by the sulphates, the phosphates, and the carbonates. Plumbic oxide, indeed, is scarcely soluble in water which contains these salts in solution. A solution of calcic carbonate in carbonic acid is especially remarkable for the preservative influence which it exerts, and as this latter is a very usual impurity in water, few spring waters act on the metal to any dangerous extent. In these cases a film of insoluble plumbic carbonate is formed upon the surface, and the metal beneath is protected from further injury. The action of water on lead is a matter of great importance in its sanitary bearings, on account of the extensive employment of this metal in cisterns and pipes for the storage and supply of water. Rain water, as collected from the roofs of houses, is for the most part sufficiently impure, especially in large towns, to prevent its action upon the metal. Of all the salts of lead the hydrated basic carbonate is the least soluble, pure water not taking up more than 1 part in 4 millions, or about a sixtieth of a grain per gallon. If a solution of plumbic oxide in distilled water, containing 60 or 70 milligrammes per litre, or about 4 or 5 grains to the gallon, be exposed to the air, it soon becomes filled with silky crystals of the hydrated basic carbonate, owing to the absorption of carbonic acid; and in a few hours the water does not contain more than  $\frac{1}{1,000,000}$  of its weight of the metal in solution. Water highly charged with carbonic acid may nevertheless dissolve lead to a dangerous extent, owing to the

solubility of plumbic carbonate in excess of carbonic acid ; when water thus impregnated with lead is boiled, the gas is expelled, and the carbonate subsides. Sometimes, as in the soft lake waters of Scotland, the presence of a little vegetable matter acts as a preservative agent by combining with a portion of oxide of lead, and forming an insoluble and closely adhering natural pigment which lines the pipes and cisterns. So general, however, is the action of water upon lead, that it is rare to find any that has been kept in cisterns of this metal perfectly free from all traces of it. Slate cisterns are therefore greatly to be preferred to leaden ones.

(896) *Uses*.—From its softness, fusibility, durability, and the ease with which it may be worked, lead is applied to a multiplicity of purposes. The reception chambers in the manufacture of sulphuric acid are lined with it. It forms the ordinary material for cisterns, water-pipes, and gutters, and is frequently employed in covering the roofs of houses.

The *alloys* of lead are numerous and important. Shot for fowling-pieces is an alloy of lead with a small proportion of arsenic, which hardens it and facilitates its granulation into globules ; the quantity of arsenic varies with the purity and softness of the lead : usually it requires from 3 to 8 parts in 1000. The common white arsenic of the shops is added to the lead, melted in a covered vessel ; the arsenious anhydride is reduced by the lead, and the oxide of lead thus formed rises as a film to the surface of the alloy. Sonnenschein observed an alloy of iron and lead ( $\text{FePb}_2$ ) which had been accidentally formed in a blast furnace, in acicular feathery crystals ; it was yellow, harder than lead, and of sp. gr. 10.36 ; it contained 11.14 per cent. of iron.

When lead is alloyed with about one-third of its weight of antimony, it forms *type-metal* : a superior variety of type consists of 1 part of antimony, 1 of tin, and 2 of lead ; it is harder and tougher than the common alloy used for this purpose. Both the alloys are sufficiently fusible to allow of being readily cast ; they expand at the moment of solidification, and copy the mould accurately ; they are hard enough to bear the action of the press, and yet not so hard as to cut the paper. The ordinary *fusible metal* contains lead, as do the various compounds called pewter, Britannia metal, and Queen's metal. The solder used by tinplate workers and plumbers is a mixture of lead and tin (812). When lead is melted with zinc, a white, hard, ductile alloy is formed ; but the two metals separate into two distinct layers if the fused mass be left to cool slowly. *Pot-metal* is an alloy of lead and

copper, obtained by throwing lumps of copper into red-hot melted lead (Brande): it is of a grey colour, brittle, and granular.

Other compounds of lead are also largely employed in the arts. The red oxide is used in large proportion in the manufacture of flint-glass (599). The carbonates, the oxychlorides, and the chromates are extensively employed as pigments.

(897) COMPOUNDS OF LEAD WITH OXYGEN.—Lead forms four oxides;—an unimportant black suboxide,  $\text{Pb}_2\text{O}$ , obtained by heating the oxalate to about  $608^\circ$  ( $320^\circ$  C.), in a glass retort. A protoxide,  $\text{PbO}$ , from which the ordinary salts of the metal are formed; a dioxide,  $\text{PbO}_2$ , which is insoluble in acids; and red lead, which is a compound of the two oxides last mentioned, usually in the proportions indicated by the formula ( $2\text{PbO}, \text{PbO}_2$ ).

*Lead oxide, Plumbic oxide, or Protoxide of lead* ( $\text{PbO} = 223$ ); *Sp. Gr.* 9.2 to 9.5; *Comp. in 100 parts*, Pb, 92.82; O, 7.18.—This oxide is well known under the name of *litharge*. Its colour varies according to the mode of its preparation. Usually it is obtained on a large scale by the oxidation of lead in a current of air, in which case it forms a scaly mass, which, if of a yellow colour, is commonly termed ‘litharge of silver;’ if redder, it is termed ‘litharge of gold.’ The former is the purer, as the red colour is due in many cases to the presence of a small quantity of minium. If the oxidation be effected at a temperature below that required for the fusion of the oxide, a yellow powder termed *massicot* is obtained. Common litharge, when reduced to a fine powder, also has a dull yellow colour; when heated, it assumes a brown-red hue, which disappears again as it cools.

If a hot solution of caustic soda, of sp. gr. 1.42, be saturated with litharge, the oxide is deposited, as the liquid cools, in beautiful anhydrous rose-coloured crystals. If the solution of plumbic oxide in caustic soda be allowed to evaporate spontaneously by exposure to the air, the alkali gradually absorbs carbonic acid, and the oxide is deposited in transparent anhydrous dodecahedral crystals.

If the salt of lead be precipitated by the addition of a caustic alkali in slight excess, the oxide of lead is precipitated in the form of a white hydrate ( $2\text{PbO}, \text{H}_2\text{O}$ ). Another hydrate ( $3\text{PbO}, \text{H}_2\text{O}$ ) may be obtained in groups of transparent octahedra, or of four-sided prisms mixed with anhydrous crystals, by precipitating a solution of tribasic plumbic acetate by an excess of ammonia, at a temperature of  $86^\circ$  ( $30^\circ$  C.).

Both litharge and the hydrated oxide of lead absorb carbonic acid slowly from the atmosphere.

Plumbic oxide fuses at a heat above redness, and crystallizes on cooling in semi-transparent scales. When fused, it combines rapidly with the earths and with silica, speedily destroying and penetrating the crucibles in which it is melted. It should not be fused in platinum crucibles, since it becomes decomposed into

the dioxide, and metallic lead; the latter attacking and spoiling the crucible. The protoxide is slightly soluble in water, to which it communicates an alkaline reaction. The presence of a very small quantity of saline matter diminishes or prevents the solution of this oxide; the solution absorbs carbonic acid rapidly from the air, and mere filtration in many cases causes the deposition of a large portion of the oxide in the form of hydrated basic carbonate.

Oxide of lead is soluble in solutions of the caustic alkalies; indeed it forms compounds with the alkalies and alkaline earths, which have been obtained in crystals; they are, however, decomposed by simple exposure to the atmosphere, owing to the absorption of carbonic acid. The solution of the oxide in lime-water is sometimes used as a hair-dye: the lime softens and partially decomposes the hair, and the lead of the oxide, combining with the sulphur of the hair, forms plumbic sulphide, which stains the hair of a permanent black. Litharge is in continual requisition by the assayer as a flux; it also enters largely into the composition of the glaze of common earthenware. A mixture of 1 part of masticot with 8 or 10 of brick-dust, made into a paste with linseed oil, forms *Dhil mastic*: it sets exceedingly hard, and is frequently employed to repair defects in stone facings; the stone should be moistened before applying the mastic.

Plumbic oxide is a powerful base. It has a strong tendency to form basic salts; those which it yields with acetic acid, and some of those with nitric acid, are soluble: they exert a strongly alkaline reaction upon test-paper, and absorb carbonic acid with avidity. Indeed, owing to the very sparing solubility of the basic carbonate of lead, a solution of a basic salt of lead is the most delicate test for the presence of carbonic acid, either in a gas or in distilled water; a mere trace of carbonic acid occasions the formation of the peculiar silky crystalline precipitate which characterizes the basic hydrated plumbic carbonate.

(898) *Minium*, or *Red lead* (*sp. gr.* about 9·08), is a compound of protoxide of lead with the dioxide. It was obtained by Berzelius as  $\text{PbO}, \text{PbO}_2$ , but its most usual composition is represented by the formula  $2\text{PbO}, \text{PbO}_2$ , though well crystallized samples have been formed, which consisted of  $3\text{PbO}, \text{PbO}_2$ . All these compounds possess a brilliant red colour. If the latter two be treated with a solution of potash, or with one of normal plumbic acetate, the excess of plumbic oxide may be dissolved out, and the compound  $\text{PbO}, \text{PbO}_2$  is left.

Red lead is obtained by heating metallic lead, so as first to

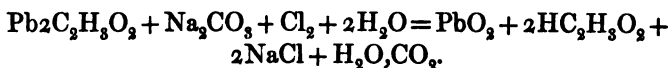
procure the protoxide or massicot, keeping the temperature below the fusing-point of the oxide; the oxide so obtained is finely levigated in water, and the particles which are held in suspension are allowed to subside, dried, and exposed, in iron trays, to a heat of about  $608^{\circ}$  ( $320^{\circ}$  C.), in a reverberatory furnace. The additional quantity of oxygen is gradually absorbed. If white lead is submitted to a similar roasting, the carbonic anhydride is expelled, leaving protoxide of lead, which is converted into minium of very fine quality by the gradual absorption of oxygen. The principal use of red lead is in the manufacture of flint glass. Much care is required in the preparation of minium for this purpose: it is necessary that it should be free from the oxides of other metals, which would impart colour to the glass. In the oxidation of the lead, which constitutes the first stage in the preparation of red lead, the metals which are more oxidizable than lead are removed with the first portions of oxide; whilst the copper and silver accumulate in the portions of oxide which are produced last. The intermediate stage of the operation is therefore that which furnishes the purest oxide. Minium is better suited to the glass-maker than litharge, because the excess of oxygen burns off any combustible matter which may accidentally be present, and converts the ferrous into ferric oxide. Red lead is also used for colouring the inferior kinds of red sealing-wax, and for paper-staining.

If minium be exposed to a high temperature it is decomposed, oxygen is evolved, and the protoxide of lead remains. Minium is insoluble in the acids, but by many of them, especially by nitric acid, it is decomposed; a salt of the protoxide is formed, and the brown dioxide remains behind.

(899) *Plumbic dioxide*, or *Peroxide of lead* ( $\text{PbO}_2 = 239$ ); *Sp. Gr.* 9.45; *Comp. in 100 parts*, Pb, 86.61; O, 13.39.—This compound is occasionally found native in iron-black brilliant hexahedral prisms, forming *heavy lead ore*. It is usually prepared by levigating minium very finely, and digesting the powder in boiling nitric acid, diluted with 4 or 5 times its bulk of water; the residue is washed with fresh nitric acid, and then with water, till everything soluble is removed. It may also be obtained by fusing at a gentle heat a mixture of 4 parts of litharge in fine powder, with 1 part of potassic chlorate and 8 parts of nitre, and washing the product with water. Wöhler prepares the dioxide by transmitting a current of gaseous chlorine through the magma obtained by mixing a solution of 4 parts of plumbic acetate with a solution of 3 parts of crystallized sodic carbonate: the plumbic



carbonate becomes gradually but completely converted into dioxide, and must be thoroughly washed; sodic chloride is formed, and acetic and carbonic acids are set free, as follows:—



Various other oxidizing agents may be employed to convert the plumbic protoxide into dioxide: *e.g.* plumbic acetate when heated with a solution of bleaching-powder yields the dioxide in crystals.

Plumbic dioxide is insoluble in water and in acids; it is converted by heat under disengagement of oxygen into the protoxide; sulphurous anhydride instantly decomposes it, forming plumbic sulphate;  $\text{PbO}_2 + \text{SO}_2 = \text{PbSO}_4$ ; hence it is frequently employed in the laboratory to absorb sulphurous anhydride when mixed with other gases.

If digested in a solution of ammonia, or subjected to a current of the gas, mutual decomposition occurs; water, ammoniac nitrate, and plumbic oxide are formed. Cold diluted hydrochloric acid dissolves this oxide, forming a rose-coloured solution, from which the caustic alkalies reprecipitate the dioxide; but if the acid be employed hot, or in a concentrated form, plumbic chloride is produced, and chlorine is set free. If the dioxide be mixed with a fifth of its weight of sulphur, the mixture takes fire by friction, sulphurous anhydride and plumbic sulphide being produced.

Plumbic dioxide appears to possess feebly acid properties. By fusing the pure dioxide with excess of caustic potash or soda, in a silver crucible, and dissolving the residue in a small quantity of hot water, crystals of potassic or sodic *plumbate* are formed as the solution cools: potassic plumbate consists of  $\text{K}_2\text{PbO}_3, 3\text{H}_2\text{O}$  (Freymy). Pure water decomposes these compounds, and the plumbic dioxide subsides. Like the peroxides of silver and manganese, plumbic peroxide is a conductor of electricity, and is formed at the zincode of the battery when aqueous solutions of the ordinary plumbic salts are decomposed by the voltaic current.

(900) COMPOUNDS OF SULPHUR WITH LEAD.—The most important of these is the protosulphide,  $\text{PbS}$ , the *galena* of mineralogists. Besides this a subsulphide,  $\text{Pb}_2\text{S}$ , is formed as the *lead matt* in reducing galena; and a red persulphide is also obtainable, though its composition is not accurately known: it is quickly resolved in the liquid into protosulphide of lead and free sulphur. This persulphide is procured by adding a solution of a persulphide of one of the metals of the alkalies to a solution of a salt of lead.

*Plumbic sulphide, Protosulphide of lead, or Galena* ( $\text{PbS} = 239$ ); *Sp. Gr.* 7.59: *Comp. in 100 parts*, Pb, 86.61; S, 13.39.—Galena is an abundant mineral, and forms the principal ore of lead: it is a brittle substance, and is found crystallized, more or less distinctly, in cubes of a deep leaden colour and strong metallic lustre. Plumbic sulphide may be formed artificially by fusing lead with sulphur; or it may be precipitated as a hydrate by treating any of its salts,

either in solution or in suspension in water, with sulphuretted hydrogen. Plumbic sulphide requires a full red heat for its fusion, and at this temperature it undergoes partial volatilization. When heated in closed vessels, part of the sulphur is expelled, and a *subsulphide*, or *plumbous sulphide* ( $Pb_2S$ ) is left: this subsulphide is formed on the large scale in the process for reducing galena; it is more fusible than the protosulphide, and may be melted at a high temperature without undergoing decomposition; but if it be heated only to the point at which it begins to soften, the subsulphide is decomposed, and metallic lead melts out, leaving the less fusible protosulphide. Galena, when heated in contact with air, is oxidated, part of the sulphur burns off, and a mixture of plumbic oxide and sulphate is formed. Nitric acid and aqua regia decompose it, converting it into sulphate: hydrochloric acid acts but slowly upon it in the cold, but at a boiling temperature it decomposes it freely and evolves sulphuretted hydrogen. When this sulphide is fused with lime or with the hydrated alkalies, metallic lead is obtained. If heated with oxide of lead or of iron, it is reduced with escape of sulphurous anhydride. When heated with a small quantity of nitre a similar result is obtained. When plumbic sulphide is heated with metallic iron it is decomposed, sulphide of iron and metallic lead being the result. Advantage is taken of this fact in the assay of galena; 10 grammes of the powdered ore are mixed with 15 grammes of black flux, 3 or 4 blacksmith's nails are placed in a Cornish crucible with their heads downwards, the mixture is introduced, and covered with a small quantity of fused and powdered borax. It is heated to full redness for 10 minutes: the nails are withdrawn, and, when cold, the crucible is broken, and the button of metallic lead is weighed. The Cornish assayers usually employ 200 grains of the ore in each trial.

(901) *Plumbic chloride*, or *Chloride of lead* ( $PbCl_2=278$ ; *Sp. Gr.* 5·8; *Comp. in 100 parts*, Pb, 74·48; Cl, 25·52), is best prepared by precipitating a solution of plumbic nitrate by the addition of hydrochloric acid, or of a solution of sodic chloride; a sparingly soluble, white, heavy precipitate occurs. It is soluble in about 33 parts of boiling water, but it is taken up more sparingly if an excess of hydrochloric acid be present; the concentrated acid, however, dissolves it readily, and deposits it in long, delicate, six-sided needles. It is easily fusible into a semi-transparent, horny, sectile mass, and at high temperatures may be volatilized. If kept fused in air till no more fumes arise, it is converted into an oxychloride ( $PbO, PbCl_2$ ). The alkalies at

first convert it into an oxychloride, and if the action be prolonged, into pure oxide.

*Oxychlorides of Lead.*—The chloride combines with oxide of lead in several proportions. One of these forms a white, translucent, fusible, colourless mineral ( $2\text{PbO}, \text{PbCl}_2$ ), *mendipite*, which is found in the Mendip Hills crystallized in right rhombic prisms. Pattinson's white oxychloride of lead ( $\text{PbO}, \text{PbCl}_2$ ) is procured by grinding galena in a closed chert mill with concentrated hydrochloric acid: sulphuretted hydrogen is liberated in large quantity, and the sparingly soluble plumbic chloride is first washed with common water, and chalk added to neutralize every trace of the acid: it is then dissolved in hot distilled water, and precipitated by the addition of lime-water in quantity just sufficient to remove half the chlorine;  $\text{CaO} + 2\text{PbCl}_2 = \text{CaCl}_2 + \text{PbO}, \text{PbCl}_2$ . This oxychloride is used to some extent as a pigment instead of white-lead. Another oxychloride ( $\text{PbCl}_2, 7\text{PbO}$ ) is a pigment of some importance, known under the name of *patent yellow*, or *Turner's yellow*; it forms a very fusible compound of a bright yellow colour, which may be obtained by heating together 1 part of sal ammoniac and 10 parts of litharge.

When an acid solution of plumbic chloride is precipitated by a current of sulphuretted hydrogen, the precipitate which is first formed is of a bright red colour, but by the further action of the gas it becomes black, and furnishes plumbic sulphide: the red compound is a *chlorosulphide* of lead ( $3\text{PbS}, 2\text{PbCl}_2$ ).

PLUMBIC BROMIDE, or *Bromide of lead* ( $\text{PbBr}_2 = 367$ ; *sp. gr.* 6.63), is white, sparingly soluble, and fusible at a red heat.

(902) PLUMBIC IODIDE, or *Iodide of lead* ( $\text{PbI}_2 = 461$ ; *Sp. Gr.* 6.384), is easily obtained by precipitating a solution of plumbic nitrate or acetate by one of potassic iodide: it is thrown down as a bright yellow powder, sparingly soluble in cold water, but more soluble in hot water; the solution as it cools deposits beautiful yellow spangles of a silky lustre; they may be fused by a moderate heat.

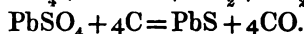
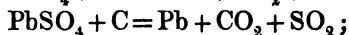
Plumbic iodide forms double salts with the iodides of the alkali-metals. Several oxyiodides of lead may also be formed.

A remarkable compound of oxyiodide of lead with carbonate of lead [ $\text{Pb}_2\text{OI}_2, 4\text{PbCO}_3$ ], of a blue colour, may be obtained by precipitating the tribasic plumbic acetate with a mixture of 1 atom of potassic biniodide ( $\text{KI}_2$ ) and 2 of potassic carbonate.

*Plumbic fluoride*, or *Fluoride of lead* ( $\text{PbF}_2$ ), is white, insoluble, and fusible.

(903) PLUMBIC SULPHATE, or *Sulphate of lead* ( $\text{PbSO}_4 = 303$ ; *Sp. Gr.* 6.30; *Comp. in 100 parts*,  $\text{PbO}, 73.61$ ;  $\text{SO}_3, 26.39$ ).—This compound occurs native in white prismatic or octohedral crystals; it is also found in combination with plumbic carbonate.

When procured artificially, it forms a white powder, slightly soluble in nitric acid, freely so in a solution of ammoniac acetate of sp. gr. 1.060, or upwards. An excess of sulphuric acid, however, throws down nearly the whole of the lead as sulphate from the acetic solution. The other salts of ammonium also possess the property of dissolving plumbic sulphate, but to a smaller extent. They form double salts with plumbic sulphate, and these compounds are slightly soluble. Plumbic sulphate is dissolved also, to some extent, by concentrated sulphuric acid, but it is insoluble in pure water. Hot hydrochloric acid likewise dissolves it sensibly, and deposits crystals of plumbic chloride on cooling, leaving a portion of sulphuric acid free in the solution. It may be obtained by adding sulphuric acid, or a solution of any sulphate, to a solution of one of the salts of lead. It is furnished in large quantities as a secondary product during the preparation of aluminic acetate. Like all the insoluble compounds of lead, it is gradually decomposed by sulphuretted hydrogen; a black plumbic sulphide is formed, and the acid is set free. Before the blowpipe it yields metallic lead in the reducing flame, though it will bear a high temperature without decomposition when heated alone. Plumbic sulphate and sulphide when heated together decompose each other, as explained when speaking of the process of lead smelting (890). The sulphate is reduced when heated with carbon, but the products vary with the proportion of carbon used, as may be seen by the annexed equations:—



*Plumbic Sulphite* ( $\text{PbSO}_3$ ) is a white powder, insoluble in water, but soluble in acids with escape of sulphurous acid: when heated it is partially decomposed, with escape of sulphurous anhydride.

(904) **NITRATES OF LEAD.**—Plumbic oxide forms several salts with nitric acid, viz.,  $\text{Pb}_2\text{NO}_3$ ;  $\text{Pb}_2\text{NO}_3, \text{PbOH}_2\text{O}$ ;  $2(\text{Pb}_2\text{NO}_3, 2\text{PbO}), 3\text{H}_2\text{O}$ ; and  $2(\text{Pb}_2\text{NO}_3, 5\text{PbO}), 3\text{H}_2\text{O}$ .

*Plumbic nitrate*, or *Nitrate of lead* ( $\text{Pb}_2\text{NO}_3 = 331$ ); *Sp. Gr.* 4.40; *Comp. in 100 parts*,  $\text{PbO}$ , 67.22;  $\text{N}_2\text{O}_5$ , 32.78.—This, the normal nitrate, is easily formed by dissolving litharge or metallic lead in an excess of nitric acid somewhat diluted: it crystallizes in regular anhydrous octohedra, which are sometimes transparent, but more commonly milk-white and opaque. It is soluble in about 8 parts of cold water, is sparingly soluble in nitric acid, and insoluble in alcohol. If heated to redness, it decrepitates strongly, then fuses and is decomposed; oxygen, and nitric per-

oxide ( $\text{NO}_2$ ), in the anhydrous state, are evolved (367), while plumbic oxide remains.

Caustic ammonia, if added to a solution of the nitrate, in quantity insufficient to combine with the whole of the acid, throws down a sparingly soluble *dibasic plumbic nitrate* ( $\text{Pb}_2\text{NO}_3, \text{PbO}, \text{H}_2\text{O}$ ). This salt may be also procured by boiling the normal nitrate with litharge. It is said to be deposited from its solution in hot water, in small opaque anhydrous crystals, which decrepitate forcibly when heated; I have, however, always found it to crystallize in leaflets with  $\text{H}_2\text{O}$ , and this accords with Péligot's observation. By precipitating the nitrate with a slight excess of ammonia, a *tribasic nitrate* is formed, which falls as a white powder, containing  $1\frac{1}{2}\text{H}_2\text{O}$ ; by adding a large excess of ammonia to the normal nitrate, a *hexanitrate* is formed; it also contains  $1\frac{1}{2}\text{H}_2\text{O}$  (Berzelius).

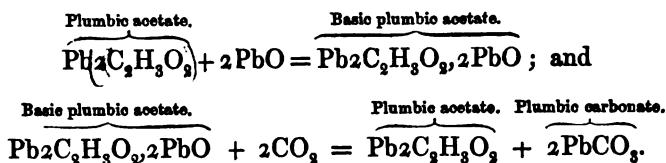
(905) NITRITES OF LEAD.—The action of metallic lead on a solution of normal plumbic nitrate is remarkable; the solution of the normal salt dissolves the metal without evolution of gas, whilst basic salts of the lower oxides of nitrogen are produced. Several of these compounds may be obtained; the composition of the basic salt varying according to the proportions of the normal nitrate and of the metal employed. When a solution of 331 parts, or 1 equivalent of normal plumbic nitrate, is heated to about  $140^\circ$  ( $60^\circ \text{C.}$ ), with 207 parts or 1 equivalent of metallic lead, perfect solution takes place, and a salt having the formula ( $2\text{PbNO}_2, \text{H}_2\text{O}$ ) crystallizes on cooling, in yellow plates; for  $\text{Pb}_2\text{NO}_3 + \text{Pb} = 2\text{PbNO}_2$ . If  $1\frac{1}{2}$  equivalent of lead be employed instead of 1 equivalent, another salt, composed of ( $4\text{PbNO}_2, 3\text{PbOH}_2\text{O}$ ), crystallizes in heavy orange-red needles. By boiling a very dilute solution of the nitrate with 2 equivalents of lead for some time, a third salt, which is a *tetrabasic-nitrite of lead*, composed of ( $\text{Pb}_2\text{NO}_3, 3\text{PbO}, \text{H}_2\text{O}$ ; Péligot), crystallizes in hard rose-red silky needles, which are but sparingly soluble in hot water, and still less so in cold: a normal plumbic nitrite,  $\text{Pb}_2\text{NO}_2$ , may be formed by transmitting a current of carbonic acid through the solution of the basic nitrite just mentioned: a dibasic nitrite,  $\text{Pb}_2\text{NO}_2, \text{PbO}, \text{H}_2\text{O}$ , as well as a tribasic nitrite,  $\text{Pb}_2\text{NO}_2, 2\text{PbO}$ , have also been formed.

(906) PHOSPHATES OF LEAD.—The salts of lead give a white precipitate with the soluble salts of each modification of phosphoric acid; these phosphates are principally interesting as furnishing an easy means of procuring the hydrates of these different acids, by suspending the corresponding salt in water, and decomposing it by means of a current of sulphuretted hydrogen. All the phosphates of lead are soluble in nitric acid. *Plumbic pyrophosphate* ( $\text{Pb}_3\text{P}_2\text{O}_7$ ), before the blowpipe furnishes a semi-transparent globule, which becomes remarkably crystalline on cooling. *Triplumbic diphosphate* occurs both massive and crystallized in six-sided prisms; the produce of a small mine at Wissembourg consists principally of this compound, mixed with plumbic carbonate. A *chlorophosphate of lead* [*pyromorphite*,  $\text{PbCl}_2, 3(\text{Pb}_2\text{PO}_4)$ , *sp. gr.* 7.01] is found native in yellow six-sided prisms: it is readily fusible.

*Boracic anhydride* may be fused with plumbic oxide in all proportions; borate of lead enters into the composition of Faraday's optical glass. The *silicates of lead* enter largely into the formation of flint glass. Silica and plumbic

oxide may be fused together in almost all proportions; the larger the proportion of silica the less fusible is the compound, and the freer from colour: with an excess of oxide the glass is yellow.

(907) CARBONATES OF LEAD.—Native plumbic carbonate ( $\text{PbCO}_3$ ; *sp. gr.* 6.46) is a beautiful mineral met with crystallized in transparent needles, or in fibrous masses, which are generally opaque. It is soft and brittle, and usually accompanies the deposits of galena, in small quantity. The manufacture of plumbic carbonate, or *white lead*, for the painter, is carried on upon a large scale. Several methods are in use in the preparation of this compound: in all of them, however, certain peculiarities in the properties of the acetates of lead are taken advantage of. There are two plumbic acetates—a normal salt,  $\text{Pb}_2\text{C}_2\text{H}_3\text{O}_5$ , and a basic acetate ( $\text{Pb}_2\text{C}_2\text{H}_3\text{O}_5, 2\text{PbO}$ ). A solution of the normal acetate in the presence of an excess of plumbic oxide readily unites with it to form the basic salt, and this basic acetate, if exposed to an atmosphere containing carbonic anhydride, rapidly absorbs this gas, and is thus converted into plumbic carbonate and normal acetate. These changes may be thus represented:—



The following is the plan which is known as the Dutch method of making white lead: it is still carried on extensively at Lille:—A number of small glazed earthen pots are partially filled with a weak malt vinegar, and in each pot a thin sheet of cast lead coiled into a spiral form is placed; these pots are then imbedded in spent tan, arranged in rows, and covered with boards; thus prepared, they are placed in tiers one above another to a depth of 18 or 20 feet,—the warmth given out during the putrefaction of the tan volatilizes the vinegar, and, under the united influence of the air and acid fumes, plumbic oxide is formed upon the surface of the coils of metal; this oxide reacts upon the acetic acid which rises in vapour from the vinegar, and a basic plumbic acetate is thus produced. The carbonic anhydride which is supplied from the decomposing hot-bed readily converts this salt into plumbic carbonate and the normal acetate; whilst the latter again combines with a fresh portion of newly-formed oxide, and produces the basic acetate, which is decomposed as before: successive decompositions and recompositions ensue, as the normal acetate imme-

diately dissolves any plumbic oxide presented to it, forming the basic acetate, which again is decomposed under the influence of carbonic anhydride. Rolled lead cannot be advantageously substituted for cast lead in this process, and the purest lead is always preferred, traces of iron being sufficient to impart an objectionable yellow tinge to the product.

Since the lead in this process derives oxygen from the air, it is necessary that the atmosphere be allowed to come sufficiently into contact with the coils. The quantity of vinegar which is required is very small, 1 part of pure acetic acid to 100 parts of lead being amply sufficient. The carbonate is thus produced very slowly, and forms a compact layer upon the surface of the coils. It always contains an excess of hydrated plumbic oxide, but the proportion of this oxide is liable to vary. Mulder found a specimen which he examined, to contain  $\text{PbOH}_2\text{O}_3\text{PbCO}_3$ ; but more usually it consists of  $\text{PbOH}_2\text{O}_2\text{PbCO}_3$ . On unrolling the coils, the carbonate breaks off in flakes of a dead-white colour, furnishing the kind of white lead most approved by artists and colourmen. Before it is fitted for their use, it is subjected to the processes of grinding and levigation, by which it is reduced to an impalpable powder. Although this pulverization is performed under water, the fine particles of the carbonate become diffused through the air, rendering the operation very deleterious to the workmen.

This circumstance, combined with the length of time requisite for the formation of the carbonate, induced Thénard to substitute for the foregoing process the direct decomposition of a solution of the basic plumbic acetate, by means of a current of carbonic anhydride; the carbonate is thus procured in a state of extreme division, and as rapidly as can be desired: it has, however, less opacity, or body, owing to its being deposited in exceedingly minute crystals, and is inferior as a pigment to that procured by the Dutch method.

A third process, at one time employed at Birmingham, consisted in exposing litharge, moistened with a solution of normal plumbic acetate, to a current of impure carbonic anhydride, obtained from the combustion of coke.

Plumbic carbonate is easily decomposed by heat, giving off carbonic anhydride, and leaving a residue of plumbic oxide. It is insoluble in water, unless the water be charged with carbonic acid to a large extent, when it is slightly soluble. It is also soluble in most of the acids with effervescence, and is likewise dissolved by solutions of potash and soda. It is quickly blackened

by exposure to sulphuretted hydrogen both in the form of gas and when in solution in water. This liability to blacken by the action of the gas is possessed by all the salts of lead, in common with the carbonate, and is a serious objection to the use of the compounds of lead in pigments.

White lead is often fraudulently mixed with a considerable quantity of baric sulphate, which is much cheaper, though its whiteness is less intense; a small quantity of indigo, charcoal, or plumbic sulphide, is usually added to white lead, in order to substitute a bluish tint for the natural tendency of the white towards yellow.

(908) CHARACTERS OF THE COMPOUNDS OF LEAD.—The salts of lead with colourless acids are colourless. The soluble salts, even when neutral in composition, redden litmus; but its basic salts have an alkaline reaction. They have a sweetish metallic taste and exert a poisonous action on the system. In cases of poisoning by a dose of the soluble salts of lead, the best antidote is magnesian or sodic sulphate, which, by double decomposition, forms the insoluble and inert plumbic sulphate. This, however, is of no avail in the more usual forms of lead poisoning, in which the metal is introduced in minute quantities, unintentionally, in water, or in articles of diet.

The best tests for lead are the formation of a white insoluble sulphate when *sulphuric acid* or any of the soluble *sulphates* are added to its solutions; this precipitate is insoluble in potassic cyanide and in acetic acid, but slightly soluble in nitric acid, more readily soluble in excess of caustic potash, freely soluble in ammoniac acetate; a black sulphide with *sulphuretted hydrogen* and with *ammoniac hydrosulphide*, insoluble in excess of the precipitant and in solutions of the alkalies; a yellow chromate with *potassic chromate*; and a yellow iodide with *potassic iodide*. *Hydrochloric acid* and the soluble chlorides give in moderately diluted solutions of lead, a white crystalline precipitate of plumbic chloride, readily soluble in excess of potash. *Caustic potash* gives a white precipitate of the hydrated oxide, which is redissolved in an excess of the fixed alkalies, but is nearly insoluble in ammonia. *Potassic* or *sodic carbonate* gives a dense white precipitate of white lead, which is insoluble in excess of the precipitant. Many other insoluble white salts may be formed, as the phosphate, arseniate, the ferrocyanide, and the cyanide: the latter is insoluble in excess of potassic cyanide, but soluble in diluted nitric acid. All the insoluble salts of lead are soluble in a solution of caustic potash.



Lead has a remarkable tendency to form basic salts, but the number of its double salts is not great. From the insolubility of many of its organic compounds, it has been much used to determine the combining proportion of organic bodies. It is, however, more advantageous to employ silver for this purpose, because plumbic oxide is to a small extent volatile.

Lead, like most other metals of comparatively weak attraction for oxygen, is easily precipitated from its solutions in the metallic state, by the metals more oxidizable than itself: if, for instance, a piece of zinc be suspended in a solution containing a compound of lead, such as plumbic acetate, crystals of lead are deposited in a beautiful arborescent form.

*Before the blowpipe* on charcoal the salts of lead yield a soft white malleable bead of the metal, surrounded by a yellow ring of oxide.

(909) *Estimation of Lead.*—Lead is generally estimated in the form of the sulphate, which contains 68.31 per cent. of the metal. More rarely it is determined from the protoxide, of which 100 parts correspond to 92.82 of lead: porcelain crucibles must be employed for these experiments, since plumbic oxide is easily reduced to the metallic state, in which case it would form an alloy with platinum, and would ruin a crucible composed of this metal.

Lead may be separated by means of sulphuric acid from all the metals, except its insoluble combinations with the metallic acids. The following is the method to be adopted:—If a galena or an alloy of lead is to be analysed, it should be treated with concentrated nitric acid until it is completely decomposed, and then evaporated nearly to dryness with a small excess of sulphuric acid; the nitric acid is thus expelled, and the metals are converted into sulphates; the mass is treated with water, which dissolves out all the metals except lead, tin, and antimony: quartz and insoluble silicates, as well as baric sulphate, if present, would also be contained in this insoluble portion. The insoluble residue is collected and weighed, and then digested repeatedly in a solution of ammoniac acetate of sp. gr. 1.065; after which the residue is again washed, dried, and weighed: the difference indicates the proportion of plumbic sulphate, which is dissolved out from the oxides of antimony and tin, and from the quartz and baric sulphate. The lead may be obtained from its solution in the ammoniac acetate by the addition of ammoniac hydrosulphide: and the plumbic sulphide thus precipitated may be converted into sulphate by means of a mixture of nitric and sulphuric acids. It is evaporated down to dryness, dried, ignited, and weighed.

The salts of lead with the metallic acids may be decomposed by fusing them with a mixture of caustic potash and potassic carbonate: the metallic acid forms a salt with potassium, and may be dissolved by the addition of water, whilst a portion of plumbic oxide is left.

§ III. THALLIUM:  $Tl = 204$ . *Sp. Gr.* 11·81 to 11·91; *Fusing-point*,  $561^{\circ}$  ( $294^{\circ}$  C.); *usually Monad*, as in  $TlCl$ ; *sometimes Triad*, as in  $TlCl_3$ .

(910) THIS metal was discovered by Crookes in 1861 (*Phil. Mag.* IV. xxi. p. 301), as he was examining the spectrum reactions of a seleniferous deposit from the sulphuric acid manufactory of Tilkerode in the Hartz; and in the following year it was obtained more abundantly from a similar source in Belgium by Lamy, to whose paper (*Ann. de Chimie*, III. lxvii. 385) the reader is referred for details, and to those of Crookes, *Phil. Trans.* 1863, and *Journ. Chem. Soc.* 1864, p. 112.

The first indication of its presence was furnished by the occurrence of a single brilliant green line nearly coincident with one of the inconspicuous lines of the barium spectrum, Ba  $\delta$  (p. 180, part I. fig. 83 Tl  $\alpha$ ). This green colour suggested to Crookes the name of *thallium* (from  $\theta α λ λ \acute{o} \varsigma$ , a budding twig). In the secondary current of an induction-coil, additional lines make their appearance (*Proceed. Roy. Soc.* 1863, xii. 407).

Thallium occurs but sparingly, and has hitherto been principally obtained from the Spanish, Belgian, and Bolivian pyrites. Its compounds have been met with by Bunsen in the mother-liquor of a spring from the Hartz, as well as in some other mineral waters, and particularly in that of Nauheim, in the mother-liquor of which Böttger found it associated with chlorides of cæsium and rubidium. Schrötter has also found it in a mica from Zinnwald and in certain samples of lepidolite.

Pure thallium is a heavy diamagnetic metal, having a strong resemblance to lead in physical properties, though its specific gravity is a little higher. The specific heat of thallium is 0·03355, Regnault (or 0·0325, Lamy), hence the metal, as its compounds show, is of the same class with silver, which it in some of its reactions resembles: like silver and the metals of the alkalis, it is a monad element. Its atomic volume is 17·2. The freshly cut surface of thallium has a bluish-white lustre, resembling that of zinc, but it tarnishes quickly by exposure to the air, and a thin film of oxide is formed. It is sufficiently soft to take impressions from the nail; it may be hammered into foil,

and pressed into wire, though its tenacity is small. If rubbed upon paper it leaves a bluish trace resembling that produced by lead, but the streak soon oxidizes and becomes yellowish. It melts at  $561^{\circ}$  ( $293^{\circ}.9$  C.; Crookes),  $554^{\circ}$  ( $290^{\circ}$  C.; Lamy), oxidizes rapidly in the air, and if heated to about  $598^{\circ}$  ( $315^{\circ}$  C.) in oxygen it takes fire and burns with an intense pure green light. The metal does not appear to be sensibly volatile below a red heat. If heated with chlorine it burns vigorously in the gas, and it also combines directly with bromine, with iodine, with sulphur, and with phosphorus. Nitric acid attacks thallium with great energy; diluted sulphuric acid also dissolves it quickly with evolution of hydrogen; but the action of hydrochloric acid, even when boiled upon it, is but slow, owing to the insolubility of the chloride. The tarnished metal becomes bright when plunged into water, owing to the solubility of the oxide; but the metal may be preserved in water unaltered. Thallium may be easily alloyed with most of the metals, and particularly with zinc, lead, antimony, tin, copper, silver, and platinum.

The easiest mode of extracting the metal consists in treating the thalliferous dust deposited in the flues of the sulphuric acid works before they enter the chamber, with an equal weight of boiling water, drawing off the clear liquor, and treating the undissolved portion again in like manner. The clear liquors are next mixed with a large excess of strong hydrochloric acid, by which a precipitate of impure thallious chloride is obtained. This is then washed, pressed, and decomposed by heating it with an equal weight of concentrated sulphuric acid. The acid thallious sulphate thus formed is dissolved in about 20 parts of water, filtered, and again precipitated as tolerably pure chloride by the addition of hydrochloric acid in excess. This precipitate is washed, pressed, and again converted into sulphate, by adding about two-thirds of its weight of oil of vitriol and heating till all the hydrochloric acid is expelled; a dense liquid is thus obtained, which as it cools solidifies to a white mass of acid thallious sulphate. This is dissolved in about ten times its weight of hot water, filtered, and allowed to crystallize. It may be purified by recrystallization, and if the solution be decomposed by metallic zinc, or by the voltaic battery, pure thallium is abundantly and easily obtained. It may be melted in an iron crucible heated over a gas flame, maintaining a current of coal-gas through the crucible to prevent oxidation.

(911) *Oxides of Thallium*.—Thallium appears to form three oxides—a suboxide of unknown composition; an oxide corresponding to the principal oxide of silver,  $Tl_2O$ ; and a superior

brown oxide, possibly  $Tl_2O_3$ , formed at the positive electrode during electrolysis of thallious sulphate by a weak current.

The most important of these is *thallious oxide*,  $Tl_2O$ ; this is very soluble in water, furnishing an alkaline caustic solution which absorbs carbonic acid from the air. The solution is colourless, and by evaporation *in vacuo* furnishes groups of pale-yellow, hydrated prismatic needles, which blacken as the evaporation proceeds; when heated to about  $598^\circ$  ( $315^\circ$  C.) it becomes anhydrous and fuses to a brown liquid which becomes yellow on cooling. A solution of thallious oxide causes a precipitate in solutions of salts of magnesium, manganese, zinc, lead, iron, and many other metals, but does not redissolve the precipitate even if the thallious oxide be in excess.

*Dithallious sulphide*, or *Sulphide of thallium* ( $Tl_2S$ ) may be obtained as a brownish-black curdy precipitate, by adding ammoniac hydrosulphide to the soluble thallious salts. The precipitate is not soluble in excess of the alkaline sulphides. Thallious acetate and oxalate in neutral solutions are precipitated by sulphuretted hydrogen.

*Thallious chloride* ( $TlCl$ ) is a yellowish-white sparingly soluble compound, less soluble in hydrochloric acid than in water, sparingly soluble in ammonia. Lamy also describes three other chlorides,  $Tl_2Cl_3$  and  $TlCl_3$ , and one with still more chlorine, possibly  $TlCl_5$ . The *protiodide* and *bromide* are yellow and sparingly soluble.

*Thallious sulphate*, or *Sulphate of thallium* ( $Tl_2SO_4$ ) is a soluble salt crystallizing in anhydrous six-sided prisms which are easily fusible. With aluminic sulphate it furnishes an octohedral alum. An acid thallious sulphate exists.

*Thallious nitrate* ( $TlNO_3$ ) crystallizes in anhydrous prismatic needles which melt easily: they are insoluble in alcohol. It is readily obtained by dissolving the metal in nitric acid.

*Thallious carbonate* ( $Tl_2CO_3$ ) furnishes long flattened prismatic needles, which require about 25 parts of cold water for solution. It is easily fusible.

The *phosphate* is sparingly soluble and is fusible.

(912) The *thallious salts* are poisonous when taken internally. They are nearly colourless, when formed with colourless acids: solutions of the salts of thallium are easily decomposed by a feeble electric current, with deposition of plates of the metal upon the negative electrode. *Metallic zinc* also precipitates finely divided metallic thallium, but tin does not reduce the metal.

No precipitate is produced in solutions of the thallious sulphate or nitrate by the *hydrated alkalis*; the *carbonates* give a

precipitate only in concentrated solutions. *Sulphuretted hydrogen* gives but little precipitate in solutions of thallious nitrate, chloride, or sulphate. *Ammonic hydrosulphide* gives a brownish-black precipitate insoluble in the sulphides of the alkali-metals. *Chlorides* and *bromides* give yellowish-white sparingly soluble precipitates; the *iodides* give a reddish-yellow precipitate; *potassic cyanide*, a white precipitate soluble in excess of the precipitant; *potassic chromate*, a pale yellow precipitate soluble in diluted acids, insoluble in ammonia. With *platinic chloride* it forms a sparingly soluble double salt ( $\text{TiCl}_3, \text{PtCl}_4$ ).

(912 a) INDIUM.—In a particular variety of zinc blende found at Freiberg, Reich and Richter ascertained the existence of a substance which, when introduced into the Bunsen gas-flame and viewed by the spectroscope, discloses two bright lines in the blue and indigo, not coincident with those of any other known body. One of these lines is rather more refrangible than the blue line of strontium, the other feebler line is near the violet line of potassium, but is less refrangible than it. These reactions suggested the name of *indium* for the new body. It is a white malleable metal, of sp. gr. about 7.36, easily fusible, slowly soluble with evolution of hydrogen in hydrochloric acid. Its oxide is white and earthy-looking, insoluble in solutions of ammonia or potash, and not precipitated by sulphuretted hydrogen from acid solutions. Solutions of its salts give a white precipitate with potassic ferrocyanide, but none with the ferricyanide.

Metallic indium may be precipitated from solutions of its salts by means of zinc; and it is thrown down slowly as oxide or as carbonate by adding baric carbonate to its solutions. Indic sulphate yields a basic sulphate of the metal when boiled with a solution of sodic acetate. Indium appears to have close relations with cadmium.

*Indic oxide* is readily reduced when heated in a current of hydrogen, in which it undergoes partial volatilization. Solution of indic acetate is completely decomposed by sulphuretted hydrogen, furnishing a yellow *sulphide* of indium soluble in hydrochloric and in sulphuric acid. Hydrated oxide of the metal remains white when digested in ammonic hydrosulphide, and is not dissolved by it. The *chloride* is white, volatilizable, and deliquescent. If the metal be a monad its atomic weight is about 36; if a dyad, 72.

## CHAPTER XIX.

## GROUP VIII.—THE NOBLE METALS.

(913) IN the group of metals with which we conclude, there is a less intimate natural relationship than in any of the preceding ones. We have, for instance, in silver a monad element, in mercury a dyad, in gold a triad, and in platinum a tetrad element; whilst the relations of the remaining metals have been but incompletely ascertained.

It is, notwithstanding, convenient for the present to group them together. The following table shows in one view, some of the most important numerical constants hitherto ascertained of the metals enumerated in this division:—

Metals.	Sym- bol.	Atomic weight.	Atomic vol.	Specific heat.	Fusing point.		Specific gravity.	Electric conduct- ivity at 0° C.
					°C.	°F.		
Mercury ...	Hg	200·0	14·56	0·0319	-38·8	-37·9	13·56	1·63*
Silver ...	Ag	108·0	10·04	0·0570	1022·8	1873	10·53	100·00
Gold ...	Au	196·7	10·04	0·0324	1102·2	2016	19·34	77·96
Platinum ...	Pt	197·1	9·12	0·0324			21·53	10·53†
Palladium ...	Pd	106·5	9·12	0·0593			11·8	12·64‡
Rhodium ...	Rh	104·3	9·12	0·0580			12·1	
Ruthenium ...	Ru	104·2	9·12				11·4	
Osmium ...	Os	199·0	9·12	0·0306			21·4	
Iridium ...	Ir	197·1	9·12	0·0326			21·15	

§ I. MERCURY: ( $\text{Hg} = 200$ ). *Sp. Gr. as liquid at 0° C., 13·596; as vapour, 6·976; Monad in Mercurous salts, as  $\text{HgCl}$ ; Dyad in Mercuric salts, as  $\text{HgCl}_2$ ; Rel. wt. 100; Melting-pt.  $-37^\circ 9$  ( $-38^\circ 8$  C.); Boiling-pt.  $662^\circ$  ( $350^\circ$  C.); Atomic and Mol Vol.    §*

(914) MERCURY (*hydrargyrum*, from  $\upsilon\delta\rho\rho$ ,  $\acute{\alpha}\rho\gamma\upsilon\rho\upsilon\varsigma$ , 'liquid silver,' or *Quicksilver*) is one of the metals which have been longest known; it is found in but few localities, and occurs most frequently in the form of the sulphide (cinnabar), usually accompanied by small quantities of the metal in its native state. Occasionally it is met with combined as an amalgam with silver,

\* At  $22^\circ 8$  C.

† At  $20^\circ 7$ .

‡ At  $17^\circ 2$ .

§ The molecule of the vapour of mercury contains only 1 atom of the metal Hg, like zinc, cadmium, and other metallic dyads.

sometimes as chloride in the form of calomel, and more rarely in that of iodine. Generally speaking, its ores are found in clay-slate, or in the red sandstone underlying the coal, and not unfrequently among the coal-measures themselves. The most productive mines are those of Almaden, in Spain; very extensive and valuable deposits of cinnabar have likewise lately been found in California; and the mines of Idria, in Transylvania, have long been extensively worked. Considerable quantities are likewise raised in China and Japan, and from the mine of Huancavelica, in Peru.

*Extraction.*—The metal may be obtained from its ore either by burning off the sulphur and distilling the mercury,—a process which is applicable both to cinnabar and to the native metal; or by heating the cinnabar with some substance capable of combining with the sulphur, and forming a fixed compound, from which the mercury is separated by heat.

At Almaden, the metal is extracted by the first process. The ore employed yields about 10 per cent. of mercury. Fig. 365 shows a section of the furnace

FIG. 365.



made use of:—each furnace contains two grates; and on the lower one, *a*, provided with a chimney, *i*, a fire of brushwood is kindled; the upper grating is formed by a brick arch, *b*, perforated with numerous apertures; on this arch the sulphide rests, the poorer pieces of ore being placed at the bottom. The brushwood quickly kindles the sulphur in the ore, which afterwards by its combustion maintains sufficient heat to continue the operation without the use of any other fuel: sulphurous anhydride is formed, and the liberated mercury distils, and is condensed in wide earthen pipes, *d, d*, connected with the upper aperture, *c*, of the furnaces; these pipes are termed *aludels*. The aludels are supported on a doubly inclined plane of masonry; at the lowest point a perforation is made, to allow of the escape of the mercury into a brick channel, *e*, through which it runs into a well; the further end, *f*, of the aludels opens into a condensing chamber, in which an additional quantity of mercury is deposited in the trough, *g*: the sulphurous anhydride escapes into the air, through the chimney, *h*. Consider-

able waste of metal is incurred during this process, from the incomplete manner in which the condensation is effected. Iron pipes, however, cannot be substituted for the earthen ones, as they become corroded rapidly by the acid vapours produced in the operation.

At Idria the process of the extraction is the same in principle as at Almaden, but the condensation is effected more completely by transmitting the mercurial vapours through a succession of chambers of masonry, instead of through aludels.

Another plan which is practised in the Palatinate consists in mixing the sulphide with slaked lime, and conducting the distillation in cast-iron furnaces and retorts. The mercury is condensed in receivers partly filled with water, while calcic sulphide and sulphate remain behind in the retort:  $4\text{HgS} + 4\text{CaO} = 4\text{Hg} + 3\text{CaS} + \text{CaSO}_4$ . Iron filings also decompose cinnabar when heated with it, ferrous sulphide being formed while mercury is liberated. Experience has shown that unless the ore contain at least  $\frac{1}{8}$  of its weight of the metal, or 3·8 lb. per ton, it is too poor to be advantageously worked by the methods at present in use.

*Purification.*—If the ore contain any admixture of zinc and bismuth, small portions of these metals are liable to be distilled over with the mercury. In this case a film forms upon the surface of the fluid metal when it is agitated in contact with air. The purity of the product is easily seen by the absence of this film, and by the perfect mobility and sphericity of the globules, which do not wet the surface of non-metallic objects. Violette finds that the distillation of mercury on the large scale is much facilitated by transmitting a current of superheated steam at about  $700^\circ$  ( $371^\circ$  C.), through the retort in which the distillation is being effected. A small quantity of mercury may be speedily purified by placing it in a bottle, with a little finely-powdered loaf-sugar; the mercury should not occupy more than one-fourth of the capacity of the bottle: the bottle is then closed, and briskly agitated for a few minutes; after which the stopper is withdrawn, and fresh air is blown into the bottle with a pair of bellows, and the agitation is repeated; this is done three or four times, and the mercury is then poured into a cone of smooth writing-paper in the apex of which a pin-hole is made; the metal runs through, and leaves the powdered sugar mixed with the oxides of the foreign metals, and a considerable quantity of finely divided mercury.

Generally speaking, the mercury imported into this country is almost chemically pure. Any foreign metals which may be present in it may be removed by digesting it for some days with diluted nitric acid in the cold: the mercury should be placed in a shallow dish, so as to expose a large surface to the acid, and it should be frequently agitated; the acid exerts but little action on the mer-



cury so long as any more oxidizable metals are present. A solution of mercuric nitrate may be substituted for the nitric acid with advantage; in this case the mercury is deposited from the solution and takes the place of the other metals, which are dissolved.

(915) *Properties*.—Mercury possesses a lustre resembling that of polished silver. It is the only metal that is fluid at common temperatures. It freezes at  $-37^{\circ}.9$  ( $-38^{\circ}.8$  C.), and contracts considerably at the moment of congelation, when it crystallizes in octohedra, of sp. gr. about 14: in this state it is malleable. When heated to  $662^{\circ}$  ( $350^{\circ}$  C.) it boils, and forms an invisible, transparent vapour, of sp. gr. 6.976. The metal, at all temperatures above  $41^{\circ}$  ( $5^{\circ}$  C.), undergoes slight spontaneous evaporation. Its specific gravity at  $60^{\circ}$  ( $15^{\circ}.5$  C.), is 13.56. When pure, it is not tarnished by exposure to air and moisture at ordinary temperatures, but if heated to about  $700^{\circ}$  ( $371^{\circ}$  C.) or  $800^{\circ}$  ( $426^{\circ}$  C.) it absorbs oxygen, and is gradually converted into the red oxide. Mercury enters into combination with chlorine, bromine, and with many of the metals at ordinary temperatures. It also unites with sulphur and with iodine without the aid of heat, if triturated with them. Hydrochloric acid is without action upon the metal, either when cold or hot. Hydriodic acid and sulphuretted hydrogen are decomposed slowly by it, with evolution of hydrogen. Concentrated sulphuric acid in the cold produces no change, but when heated with it is decomposed; sulphurous anhydride being evolved, while the mercury is oxidized, and forms a sulphate by reaction with a portion of undecomposed acid. Strong nitric acid dissolves it with rapidity, extricating nitric oxide in abundance, while mercuric nitrate is formed. If the acid be dilute, and the metal in excess, the mercury is dissolved slowly, and at ordinary temperatures mercurous nitrate is the result. Mercury may be obtained in a state of extreme division, by precipitating a solution of corrosive sublimate, by means of the solution of stannous chloride: the stannous salt, if added in sufficient quantity, absorbs all the chlorine, and a grey metallic powder subsides;  $\text{HgCl}_2 + \text{SnCl}_2 = \text{Hg} + \text{SnCl}_4$ .

*Uses*.—Mercury is employed extensively in the extraction of gold and silver from their ores by the process of amalgamation; great quantities are annually sent to South America for this purpose. Its amalgams are largely employed in the processes of silvering and gilding. Mercury also combines readily with lead, copper, bismuth, tin, and zinc, forming amalgams which are easily dissolved by an excess of mercury. Joule succeeded in many cases in obtaining definite compounds of various metals with mer-

cury, by subjecting their semi-solid amalgams to hydraulic pressure, amounting to the enormous extent of 60 tons upon the square inch: with platinum 1 atom was united with 2 atoms of mercury. With silver, with copper, and with iron, the amalgams contained 1 atom of each metal: with zinc and with lead the amalgam in each case contained 1 atom of mercury with 2 atoms of the other metals, while the amalgam of tin was represented by the formula  $\text{Sn}_7\text{Hg}$ .

Mercury is also used in the preparation of vermilion, which is highly valued as a pigment, for the purity and permanence of its tint. It is indispensable in the construction of philosophical instruments; and it is well known in various forms as a valuable medicine. It exerts a powerful action upon the animal economy, producing salivation, and seriously impairing the health of the workmen exposed to its vapours, giving rise to a remarkable tremulous state, known as *mercurial palsy*, consequent upon a peculiar form of nervous debility. By trituration with saccharine or oleaginous substances, it admits of being minutely subdivided, and a small portion of it becomes oxidized, to which the active properties of blue-pill appear to be owing; the same remark applies to the mercurial ointment, and the *pulvis hydrargyri cum creta*.

(916) OXIDES OF MERCURY.—Mercury forms two oxides, the black suboxide,  $\text{Hg}_2\text{O}$ , and the red oxide,  $\text{HgO}$ : both of them form salts with acids.

*Mercurous oxide*, or *Suboxide of mercury* ( $\text{Hg}_2\text{O}=416$ ); *Sp. Gr.* 10·68; *Comp. in 100 parts*, Hg, 96·15; O, 3·85.—This oxide, though a powerful saline base, is very unstable when isolated. It is best procured by triturating finely levigated calomel with a solution of potash or of soda, and washing the black precipitate thus obtained with cold water. It must be allowed to dry spontaneously in a dark place: the oxide so obtained is anhydrous; even when dry, mere exposure to light, or a very gentle heat, is sufficient to convert it into a mixture of red oxide and the metal.

(917) *Mercuric oxide*, *Nitric oxide* or *Red oxide of mercury* ( $\text{HgO}=216$ ); *Sp. Gr.* 11·29; *Comp. in 100 parts*, Hg, 92·59; O, 7·41.—This oxide may be obtained in red scales by heating metallic mercury to  $700^\circ$  or  $800^\circ$  ( $371^\circ$  or  $426^\circ \text{C.}$ ) in a matrass: but this process is very slow, and not productive: it is more conveniently prepared by the decomposition of the nitrate by heat, and it then has a bright scarlet colour. It may also be thrown down in the form of a yellow powder, when a solution of caustic potash or soda is added to a solution of corrosive sublimate, or of mercuric nitrate. The precipitated oxide does not differ in composition

from the red crystallized form, but it enters more readily into combination; a cold solution of oxalic acid is without action on the crystallized oxide, but it converts the precipitated oxide into oxalate; and the yellow oxide when boiled with a solution of corrosive sublimate is quickly converted into the oxychloride; but this change is very slow with the crystallized variety. The yellow oxide, when boiled with potassic dichromate, yields a basic mercuric chromate,  $\text{HgCrO}_4, 2\text{HgO}$ ; but the crystallized oxide when similarly treated yields a basic salt, with a larger excess of base,  $\text{HgCrO}_4, 3\text{HgO}$  (Millon). In short, the crystallized oxide obtained by the direct oxidation of mercury, and the precipitated oxide appear to be in different allotropic conditions.

The red oxide when heated becomes nearly black, but recovers its colour on cooling; when exposed to a temperature of ignition, it is decomposed into metallic mercury and oxygen gas: owing to the volatility of the metal, this oxide may sometimes be usefully employed as an oxidizing agent in some analytical operations. This oxide is slightly soluble in water; the solution has an acrid taste, and turns syrup of violets green. It forms with baryta a soluble compound. With ammonia it produces a yellowish-white insoluble compound, the simplest formula for which is  $(\text{Hg}_2\text{H}_2\text{NO}_3)$ ; it is possessed of strong basic powers and enters into combination with acids, forming well-defined salts.

(918) *Mercuramine*.—The best method of preparing this remarkable base consists in pouring a pure solution of ammonia upon yellow precipitated mercuric oxide in a bottle which admits of being closed, to prevent the access of carbonic acid from the air; the colour of the oxide becomes paler, and eventually a yellowish-white amorphous powder is obtained, which, when washed and dried in a dark place over quicklime, forms a hydrate of the new base, containing  $(\text{Hg}_2\text{H}_2\text{N}_2\text{O}_3, 3\text{H}_2\text{O})$ . This compound was discovered by Fourcroy and Thénard, but it was first minutely examined by Millon (*Ann. de Chimie*, III. xviii. 393). In its isolated condition it is very unstable: mere exposure to the light decomposes it. When triturated in a mortar, it produces a series of small detonations. If dried *in vacuo* over sulphuric acid, it loses  $2\text{H}_2\text{O}$ ; and between  $212^\circ$  ( $100^\circ \text{C.}$ ) and  $266^\circ$  ( $130^\circ \text{C.}$ ), a third atom of water is expelled: it then becomes dark brown, and is permanent in the air, containing  $(\text{Hg}_2\text{H}_2\text{N}_2\text{O}_3)$ . Chemists are not agreed as to the probable arrangement of the elements in this base. It resembles some of the cobalt bases into the composition of which the elements of ammonia enter. It may provisionally be described under the name *mercuramine*, and contains the elements of hydrated oxide of *tetrhydrargammonium*  $(\text{Hg}''_2\text{N}_2\text{O}, 5\text{H}_2\text{O})$ .

Mercuramine is a powerful base; its hydrate  $(\text{Hg}_2\text{H}_2\text{N}_2\text{O}_3, 3\text{H}_2\text{O})$  absorbs carbonic anhydride from the air almost as rapidly as slaked lime. It is insoluble in water and in alcohol, but it decomposes solutions of the salts of ammonium and combines with the acid. Definite salts with sulphuric, nitric, oxalic, carbonic, hydrochloric, and various other acids, have been formed. On the addition of sodic or potassic hydrate to the solutions of these salts, the hydrate of the base is precipitated. The formula of the sulphate is  $(\text{Hg}_2\text{H}_2\text{N}_2\text{O}_3)\text{SO}_4$ ; that of the

chloride ( $\text{Hg}_4\text{H}_4\text{N}_4\text{O}_4\text{Cl}_2$ ; the latter salt may be obtained as a yellow precipitate by adding a solution of corrosive sublimate to a solution of ammonia in excess and washing the precipitate with boiling water (924).

(919) **SULPHIDES OF MERCURY.**—The two sulphides of mercury,  $\text{Hg}_2\text{S}$  and  $\text{HgS}$ , correspond in composition to the oxides and chlorides of the metal.

*Mercurous sulphide*, or *Subsulphide of mercury* ( $\text{Hg}_2\text{S}=432$ ) is scarcely more stable than mercurous oxide; it is procured by transmitting a current of sulphuretted hydrogen through a solution of a mercurous salt, or by triturating 16 parts of moistened sulphur with 200 of mercury; it forms a black powder, which was formerly termed *Ethiop's mineral*. It is decomposed by nitric acid; and if the dry sulphide be sublimed, it is converted into cinnabar and metallic mercury.

(920) *Mercuric sulphide*, *Sulphide of mercury*, or *Cinnabar* ( $\text{HgS}=232$ ); *Sp. Gr. of vapour*, 5·51; *of solid*, 8·2; *Mol. vol.*   ; \* *Comp. in 100 parts*, Hg, 86·21; O, 13·79.—This compound constitutes the most abundant ore of mercury. It occurs sometimes crystallized in hexahedral prisms, but more usually as a fibrous or amorphous mass, and is a product of considerable importance in the arts, forming the pigment known under the name of *vermilion*. Some portions of the native cinnabar are of a sufficiently delicate colour to be employed after mere levigation; but it is usually prepared artificially. In Holland, this manufacture is carried on to a considerable extent. The process adopted consists in triturating sulphur with about 6 times its weight of mercury, aiding the action by a gentle heat. The black mass thus procured is thrown (in successive portions, to prevent too rapid an action) into tall earthen pots, the lower parts of which have been previously brought to a red heat; the aperture at top is closed with an iron plate, and in about 32 hours after the introduction of the whole charge, the sublimation is complete: when cold, the pots are broken, and the cinnabar, which is found deposited in layers upon the upper part, is carefully removed; the cinnabar is levigated with water, and the fine powder thus obtained is sold as vermilion; an excess of sulphur

\* The vapour volume of this compound is anomalous, the three volumes of vapour having been united without condensation, instead of being, as usual, reduced to two volumes—

			<i>Sp. Gr.</i>
Hg	2 vols.	or	0·67
S	1 vol.		0·33
	3 vols.		1·00
			5·349

3 B 2

is to be avoided, as it impairs the brilliancy of the colour. Cinnabar sublimes before undergoing fusion, and forms a yellowish-brown vapour.

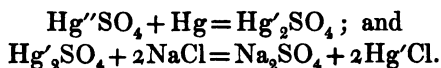
Vermilion may also be procured in the wet way, but the process is tedious, and less certain. The Chinese vermillion is supposed by some chemists to be prepared by the humid process. In order to produce vermillion by this means, Firmenich recommends the mercury to be subjected to the action of pure dipotassic pentasulphide ( $K_2S_5$ ) in the following manner:—10 parts of mercury are to be agitated for 3 or 4 hours, with 2 parts of sulphur and  $4\frac{1}{2}$  of a saturated solution of dipotassic pentasulphide; at the end of which time the mixture becomes of a dark brown colour. It is maintained for 3 or 4 days at a temperature of from  $113^\circ$  to  $122^\circ$  ( $45^\circ$  to  $50^\circ$  C.), with occasional agitation; it is next drained upon a filter, and afterwards digested with caustic soda to remove the excess of sulphur; it is thus obtained of a bright scarlet, and must then be thoroughly washed with cold water and dried. (*Chem. News*, May, 1862, p. 247.)

Mercuric sulphide is thrown down as a black precipitate by transmitting sulphuretted hydrogen through solutions of the mercuric salts: when dried and sublimed in vessels from which air is excluded, it assumes its ordinary red colour. By simple heating it becomes dark brown, and at a still higher temperature nearly black, but recovers its red colour on cooling. When heated in the open air, the sulphur burns off, and metallic mercury is liberated. It is upon this circumstance that the ordinary method of extracting the metal is founded. The pure acids are nearly without action upon cinnabar, but it is oxidized and dissolved by aqua regia. The caustic alkalies in solution do not decompose it, but if ignited with it in the dry state, a sulphate and sulphide of the alkali metal are formed, and metallic mercury sublimes;  $4HgS + 8KHO = 4Hg + K_2SO_4 + 3K_2S + 4H_2O$ . It is also decomposed if heated with metals which, like iron, zinc, and copper, have a powerful attraction for sulphur. Mercuric sulphide possesses the property of uniting with other metallic sulphides, and is slowly soluble in a solution of dipotassic sulphide; it also combines with the nitrate, the chloride, the iodide, and some other mercuric salts, forming peculiar compounds, which are produced by the action of a small proportion of sulphuretted hydrogen upon the solutions of these salts, and the production of which causes the first portions of the precipitate occasioned in them by the gas to appear white.

(921) CHLORIDES OF MERCURY.—Mercury forms two chlorides, one of which,  $HgCl$ , is well known as calomel, the other,  $HgCl_2$ , is commonly distinguished as corrosive sublimate.

*Mercurous chloride*, or *Calomel* ( $HgCl = 235.5$ ); *Sp. Gr. of vapour*, 8.35; *of solid*, 7.178; *Mol. vol.*  ; *Rel wt.* 117.75;

*Comp. in 100 parts, Hg, 84.92; Cl. 15.08.\**—This compound may be obtained by precipitating a solution of mercurous nitrate, by one of common salt; but it is more usually procured by sublimation: 13 parts of mercury are triturated with 17 of corrosive sublimate, until no metallic globules are visible, the dichloride having been previously moistened with water or alcohol, to prevent the acrid particles from being diffused through the air, the mixture is then sublimed in suitable vessels, and the calomel is deposited as a semi-transparent fibrous cake. In this operation the additional mercury combines with half the chlorine of the dichloride:  $\text{HgCl}_2 + \text{Hg} = 2\text{HgCl}$ . Sometimes the vapours are sent into a capacious chamber; the deposit then assumes the form of a fine powder. The salt may also be obtained by the decomposition of mercuric sulphate with sodic chloride. For this purpose 1 kilo. of mercury may be converted into sulphate by boiling it to dryness with 1.5 kilo. of sulphuric acid; the residue is then to be intimately mixed with 1 kilo. more of mercury, and subsequently triturated with 0.75 kilo. of sodic chloride, after which it is to be sublimed. The mercuric sulphate which is first obtained is converted into mercurous sulphate by the addition of the second portion of mercury, and this in its turn is decomposed into calomel and sodic sulphate when heated with sodic chloride:—



Calomel may also be prepared by forming a saturated solution of corrosive sublimate in water at  $122^\circ$  ( $50^\circ \text{C.}$ ), and transmitting sulphurous anhydride into the hot liquid; calomel is then precipitated in minute crystals, whilst sulphuric and hydrochloric acids are liberated;  $2\text{HgCl}_2 + 2\text{H}_2\text{O} + \text{SO}_2 = 2\text{HgCl} + 2\text{HCl} + \text{H}_2\text{SO}_4$ .

When prepared by sublimation, calomel requires careful washing and levigation, because portions of the undecomposed dichloride always sublime with the calomel, and they can only be removed by repeated washing. It was formerly supposed that the medicinal character of calomel was rendered milder by repeated sublimations. This, however, has been found to be a serious mistake, for every time that calomel is sublimed, a small portion of it is reconverted into corrosive sublimate and metallic mercury.

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\* It is possible that the formula of calomel, and of mercurous bromide and iodide should be doubled; but in that case their vapour volume would be anomalous, and would represent 4 volumes instead of 2 volumes.

*Properties.*—Calomel sublimes in quadrilateral prisms terminated by four-sided pyramids; when powdered it is of a yellowish-white colour. It begins to sublime below redness, and before undergoing fusion. Calomel is tasteless and insoluble in water; the alkalis decompose it. Sodid and potassic hydrates decompose it, whilst mercurous oxide is formed. Lime-water has a similar effect, and when mixed with a small proportion of calomel it furnishes what is known as *black wash*. Solution of ammonia forms with calomel a black compound, consisting of  $\text{Hg}_2\text{H}_2\text{NCl}$ : this change is explained in the subjoined equation;  $2\text{HgCl} + 2\text{H}_3\text{N} = \text{Hg}_2\text{H}_2\text{NCl} + \text{H}_4\text{NCl}$ . This black compound may be regarded as ammoniac chloride in which two uniequivalent atoms of mercury have taken the place of two atoms of hydrogen. Ammoniacal gas is absorbed by precipitated calomel at ordinary temperatures, and a compound containing  $(\text{HgH}_3\text{NCl})$  is formed, or ammoniac chloride in which one of the atoms of hydrogen has been displaced by a uniequivalent atom of mercury. Sulphuric acid is without action on calomel; boiling nitric acid dissolves it, and forms corrosive sublimate and mercuric nitrate; a solution of chlorine converts it slowly into corrosive sublimate; if boiled for a long time with hydrochloric acid or sodic chloride, it is resolved into corrosive sublimate and metallic mercury: the same effect is produced, but more rapidly, by boiling it in a solution of sal ammoniac.

(922) *Dichloride or bichloride of mercury; Mercuric chloride, or Corrosive sublimate* ( $\text{HgCl}_2 = 271$ ); *Sp. Gr. of vapour*, 9·8; *of solid*, 5·42; *Mol. vol.*  ; *Rel. wt.* 135·5; *Comp. in 100 parts*, Hg, 73·8; Cl, 26·2.—When heated mercury is placed in an atmosphere of chlorine it ignites from the rapid union of the gas with the metal, and the dichloride is formed. It is prepared on the large scale by mixing intimately  $2\frac{1}{2}$  parts of mercuric sulphate with 1 part of common salt, and subliming the mixture in glass vessels at a carefully regulated heat: sodic sulphate remains in the vessel, and the dichloride sublimes as represented in the equation;  $\text{HgSO}_4 + 2\text{NaCl} = \text{Na}_2\text{SO}_4 + \text{HgCl}_2$ . The fumes are extremely acrid and poisonous.

*Properties.*—Corrosive sublimate fuses at  $509^\circ$  ( $265^\circ$  C.), and boils at  $563^\circ$  ( $295^\circ$  C.); its vapours are condensed in snow-white crystalline needles, or in octohedra with a rectangular base. As sold in the shops, it occurs in transparent colourless masses, which have a crystalline fracture. It has an acrid burning taste, and disgusting metallic flavour. It is soluble in 16 parts of cold water, and in less than 3 of boiling water; on cooling it is de-

posited from a concentrated solution in transparent anhydrous quadrilateral prisms. Its solution reddens litmus; this aqueous solution, by long exposure to light, is gradually decomposed, and calomel is deposited. Alcohol when cold dissolves nearly one-third of its weight of the salt, and its own weight when boiling; ether also dissolves it freely. If an aqueous solution of corrosive sublimate be agitated with ether, almost the whole of the salt will be abstracted by it from the water, and the ethereal solution will rise to the surface. It is very soluble in solutions of the alkaline chlorides, with which it enters into combination, forming double salts.

With potassic chloride it forms three distinct crystallizable compounds,  $\text{KCl}_2\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$ ;  $\text{KCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$ ; and  $2\text{KCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$ . They are easily prepared by dissolving the salts in the proper proportions, and allowing them to crystallize. With sodic chloride only one such compound is formed,  $2(\text{NaCl} \cdot \text{HgCl}_2) \cdot 3\text{H}_2\text{O}$ . A salt with ammoniac chloride ( $6\text{H}_4\text{NCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$ ) has long been known as *sal alembroth*: it crystallizes in flattened rhomboidal tables.

Similar compounds having a composition analogous to that of the sodium salt may be formed with most of the soluble chlorides. Calcic and magnesian chlorides form more than one compound. An analogous but anhydrous salt,  $\text{HCl} \cdot \text{HgCl}_2$ , is formed by dissolving corrosive sublimate in hot hydrochloric acid, from which it crystallizes on cooling; it is, however, decomposed by water.

Mercuric chloride combines with the sulphide, and forms with it a white insoluble gelatinous compound, consisting of  $2\text{HgS} \cdot \text{HgCl}_2$ ; it is the white precipitate which is always formed at first, on passing a current of sulphuretted hydrogen through a solution of corrosive sublimate.

Corrosive sublimate is decomposed by the hydrates of the fixed alkalies and alkaline earths, a chloride of the alkali-metal and mercuric oxide being formed. When ammonia is added to a solution of corrosive sublimate, it separates only half the chlorine, uniting with the remainder to form the compound called white precipitate (924). Mercuric chloride acts powerfully on the albuminous tissues, and combines with them; it is a violent and acrid poison. The best antidote in cases of poisoning with this substance is the immediate exhibition of the whites of several raw eggs, as it coagulates the albumin, and forms with it a sparingly soluble compound. It was supposed that the dichloride was converted into calomel, but this does not appear to be the case. Owing to this action of the dichloride upon albumin, corrosive sublimate is a powerful antiseptic; a solution of this salt is hence often employed to preserve anatomical preparations: wood, cordage, and canvas, if soaked in a solution of the salt containing 1 part of it in 60 or 80 parts of water become much less liable to decay when exposed to the combined action of air and moisture.

(923) *Oxychlorides*.—Corrosive sublimate combines with mercuric oxide in



several proportions; these compounds are decomposed by the alkalis. One of these is obtained in the form of dark brown insoluble flakes ( $3\text{HgO}, \text{HgCl}_2$ ), when the dichloride is boiled with mercuric oxide. Another,  $2\text{HgO}, \text{HgCl}_2$ , is obtained in blackish scales by acting with a solution of chlorine on mercuric oxide (Thaulow). The mercuric oxychlorides are interesting, from the observations of Millon upon them, which seem to prove the persistence of the allotropic modification in a body after it has entered into combination. (*Ann. de Chimie*, III. xviii. 333.)

The three oxychlorides described by Millon consist of ( $2\text{HgO}, \text{HgCl}_2$ ), ( $3\text{HgO}, \text{HgCl}_2$ ), and ( $4\text{HgO}, \text{HgCl}_2$ ). They may all be produced by the action of potassic carbonate upon a solution of corrosive sublimate. The first may be obtained in three different isomeric conditions, the second in two, and the third in three. The action of the carbonates of the alkali-metals upon solutions of corrosive sublimate is peculiar. The addition of a solution of sublimate to a solution of pure *normal* potassic or sodic carbonate is attended with the precipitation of yellow mercuric oxide. If the mercurial solution be added to a solution of an alkaline *acid-carbonate* (bicarbonate), a red oxychloride is formed; and if even a small quantity of the acid-carbonate of the alkali-metal be mixed with a large proportion of normal alkali carbonate, this red precipitate is produced at first. This reaction may serve to distinguish the carbonates from the acid-carbonates in solution. If a cold saturated solution of potassic acid-carbonate be added gradually to 8 or 10 times its volume of a cold saturated solution of sublimate, a light granular amorphous precipitate of a bright brick-red colour is formed ( $2\text{HgO}, \text{HgCl}_2$ ). If the volume of the solution of sublimate be only 3 or 4 times as great as that of the acid-carbonate, a precipitate of similar composition is formed, but it is dense, crystalline, and red, purple, or violet in colour. Both these modifications, when decomposed by caustic potash, yield *yellow* mercuric oxide; but if 1 volume of the solution of acid-carbonate be added to 2 volumes of the solution of sublimate, stirring briskly, a jet black crystalline precipitate is formed, which also consists of  $2\text{HgO}, \text{HgCl}_2$ , but which yields the *red crystalline* mercuric oxide when decomposed by hydrated potash.

If equal volumes of the solutions be mixed, golden-yellow plates, which gradually become brown or yellowish, are deposited ( $3\text{HgO}, \text{HgCl}_2$ ). The same body may also be obtained in the amorphous form.

The tetrabasic oxychloride ( $4\text{HgO}, \text{HgCl}_2$ ) may be obtained by adding a solution of corrosive sublimate to a large excess of the solution of the acid-carbonate. Carbonic acid gradually escapes, and brown crystalline crusts are deposited: caustic potash causes the separation of *red* mercuric oxide from this compound. This oxychloride may also be obtained in the form of a brown amorphous deposit, and in golden-yellow plates; both these varieties yield the *yellow oxide* when decomposed by hydrated potash. The first two oxychlorides are converted by boiling them with water into the tetrabasic form, which is deposited from the solution in golden-yellow scales. Other oxychlorides, with 5 and with 6 atoms of mercuric oxide, are described by Roucher (*Ann. de Chimie*, III. xxvii. 353).

(924) *Action of Ammonia on Corrosive Sublimate*.—When a solution of corrosive sublimate is added to a solution of ammonia in excess, one-half of the chlorine only is removed from the salt, and the so-called *white precipitate* is formed, which, when washed with cold water, is completely soluble in nitric and in hydrochloric acid, and which therefore can contain no calomel;  $\text{HgCl}_2 + 2\text{H}_3\text{N} = (\text{Hg}''\text{H}_2\text{N}_2\text{Cl}) + \text{H}_4\text{NCl}$ . Kane considered this white precipitate as a compound of chloride with amide of mercury,  $\text{HgCl}, \text{H}_2\text{N}$ ;

but it may also be regarded as ammoniac chloride, in which 2 atoms of hydrogen are displaced by the bivalent atom of mercury ( $\text{Hg}''\text{H}_2\text{N}_2\text{Cl}$ ). If ammonia be added drop by drop to a solution of corrosive sublimate, which is purposely maintained in considerable excess, the precipitate consists of  $(\text{Hg}_4\text{H}_4\text{N}_2\text{Cl}_6)$ ; this formula would be that of mercuramine chloride, in which the place of the oxygen contained in the base is supplied by an equivalent amount of chlorine.

White precipitate has been made the subject of numerous experiments. If it be heated to about  $608^\circ$  ( $320^\circ \text{C.}$ ), ammonia and the ammoniated chloride of mercury are expelled; and a red crystalline powder remains, represented by the formula  $(2\text{HgCl}_2, \text{Hg}_2\text{N}_2)$ ; for  $6\text{Hg}''\text{H}_2\text{N}_2\text{Cl} = 3\text{H}_2\text{N} + \text{H}_2\text{N}_2, \text{HgCl}_2 + 2\text{HgCl}_2, \text{Hg}_2\text{N}_2$ . This red powder is insoluble in water and in dilute acids, but it is dissolved and decomposed by either boiling hydrochloric acid or oil of vitriol. By raising the temperature still further it is decomposed into nitrogen, metallic mercury, and calomel. It is interesting, as it appears to contain a double atom of ammonia in which the 6 atoms of hydrogen are displaced by 3 bivalent atoms of mercury.

When white precipitate is boiled in water it is decomposed, and the heavy insoluble canary-yellow mercuramine chloride is formed, whilst ammoniac chloride is formed in the solution;  $4\text{Hg}''\text{H}_2\text{N}_2\text{Cl} + 2\text{H}_2\text{O} = \text{Hg}_4\text{H}_4\text{N}_2\text{O}_2\text{Cl}_2 + 2\text{H}_4\text{NCl}$ . This yellow powder is dissolved easily by diluted nitric or hydrochloric acid.

If a solution of corrosive sublimate be added gradually to a boiling solution of sal ammoniac and free ammonia so long as the precipitate is redissolved on agitation, a compound crystallizes in rhombohedra on cooling; and the same substance is procured on boiling ordinary white precipitate in a solution of sal ammoniac. This compound fuses and undergoes decomposition at a temperature of  $572^\circ$  ( $300^\circ \text{C.}$ ); boiling water extracts a large proportion of sal ammoniac from it, and leaves the canary-yellow powder above described. It is freely soluble in acids, even in acetic acid. Kane's analysis of this compound would allow of its being represented by the formula  $\text{Hg}''\text{H}_4\text{N}_2\text{Cl}_2$ . It is sometimes called *fusible white precipitate*.

When corrosive sublimate is exposed to a current of dry ammoniacal gas, it fuses with extrication of heat; 1 atom of the salt absorbs 1 of ammonia, producing  $\text{H}_2\text{N}_2, \text{HgCl}_2$ . This compound may be sublimed without change, but it is decomposed by water: it is a true ammoniated mercuric dichloride.

The following table shows the principal compounds produced by the combined action of ammonia and heat upon corrosive sublimate:—

(1) White precipitate	...	...	$\text{Hg}''\text{H}_2\text{NCl}$ .
(2) Red crystalline compound	...	...	$2\text{HgCl}_2, \text{Hg}''\text{N}_2$ .
(3) Mercuramine chloride	...	...	$(\text{Hg}_4\text{H}_4\text{N}_2\text{O}_2)\text{Cl}_2$ .
(4) Mercuramine perchloride	...	...	$(\text{Hg}_4\text{H}_4\text{N}_2\text{Cl}_4)\text{Cl}_2$ .
(5) Fusible white precipitate	...	...	$\text{Hg}''\text{H}_4\text{N}_2\text{Cl}_2$ .
(6) Ammoniated mercuric dichloride...	...	...	$\text{H}_2\text{N}_2, \text{HgCl}_2$ .

besides the double salts, of which one is—

(7) Sal alembroth	...	...	...	$6\text{H}_4\text{NCl}, \text{HgCl}_2, \text{H}_2\text{O}$ .
(8) And another is	...	...	...	$\text{H}_4\text{NCl}, \text{HgCl}_2$ .

These remarkable compounds derive interest from their connexion with the theories which have been proposed respecting the nature of ammonia, the consideration of which will be resumed when the alkaloids or organic bases are examined.

Two BROMIDES, analogous to the chlorides of mercury may be formed; they yield corresponding double salts; both of them may be sublimed without experiencing decomposition. *Mercurous bromide* ( $\text{HgBr} = 280$ ; *sp. gr. of vapour*, 10.14; *mol. vol.* [ ]; *rel. wt.* 140) is white and insoluble. *Mercuric bromide* ( $\text{HgBr}_2 = 360$ ; *sp. gr. of vapour*, 12.16; *mol. vol.* [ ]; *rel. wt.* 180) is crystallizable and soluble.

(925) IODIDES OF MERCURY.—Mercury forms three iodides: a green iodide,  $\text{HgI}$ ; a red diiodide,  $\text{HgI}_2$ ; and an intermediate iodide ( $\text{HgI}, \text{HgI}_2$ ) of a yellow colour, obtained by precipitating mercurous nitrate by means of potassic iodide containing iodine in solution.

*Mercurous iodide* ( $\text{HgI} = 327$ ) is a green powder insoluble in water, which is easily decomposed by exposure to light, into mercury and the red iodide; the same change is effected by heating it gently with solutions of the soluble iodides or chlorides, or with hydriodic or hydrochloric acid. If heated suddenly it fuses and may be sublimed without decomposition; but if the temperature be raised gradually, it is decomposed into the red iodide and metallic mercury. It is easily formed by triturating 5 parts of iodine with 8 of mercury, moistening the mixture with a little alcohol; or it may be precipitated from a solution of any mercurous salt, by adding to it a solution of potassic iodide.

*Mercuric iodide, Biniiodide of mercury* ( $\text{HgI}_2 = 454$ ); *Mol. Vol.* [ ]; *Rel. wt.* 227; *Sp. Gr. of solid*, 6.25; *of vapour*, 15.6; *Comp. in 100 parts*, Hg, 44.05; I, 55.95.—This beautiful compound may be obtained by triturating 5 parts of iodine with 4 of mercury, and subliming the mixture; but it is procured most easily by precipitating a solution of corrosive sublimate by means of a solution of potassic iodide: the precipitate is soluble in an excess of either salt. The precipitate is at first salmon-coloured, but it speedily becomes converted into a brilliant scarlet crystalline deposit. It fuses at about  $392^\circ$  ( $200^\circ \text{C.}$ ), and yields a vapour of extraordinary density: as it cools it is deposited in yellow rhombic tables; this yellow colour is changed to red by mere agitation, or by scratching the crystals. Warington has shown that this change of colour depends upon a change in the molecular constitution of the salt, in consequence of which the rhomboidal crystals are converted into octohedra with a square base. Mercuric iodide is nearly insoluble in water, but it is taken up freely by hot alcohol. It is also dissolved by solutions of many neutral salts of ammonium, as well as by hydrochloric and hydriodic acids. With the soluble electropositive iodides it forms crystalline double salts, and it is dissolved easily by solutions of chlorides of the metals of the alkalies, but it does not form crystallizable compounds with these chlorides. A fusible double mercuric chloride and iodide ( $\text{HgI}_2, \text{HgCl}_2$ ) may be formed; and a soluble crystallizable compound ( $\text{HgI}_2, 2\text{HgCl}_2$ ) may be obtained by saturating a boiling solution of corrosive sublimate with the

mercuric iodide, and allowing it to crystallize. By adding a mixture of potassic hydrate and ammonia to a solution of mercuric iodide in one of potassic iodide, a brown powder is deposited, to which Nessler assigns the composition  $\text{Hg}_2\text{NI}, \text{H}_2\text{O}$  (624). Mercuric iodide also forms definite compounds with the oxide, and with the sulphide, of the metal.

(926) *Nitride (P) of Mercury*.—Plantamour states, that by transmitting in the cold a current of dry ammoniacal gas over the dried yellow mercuric oxide precipitated from its salts by an alkali, so long as the gas is absorbed, and then heating the dark brown mass cautiously to a temperature not exceeding  $302^\circ$  ( $150^\circ \text{C.}$ ), so long as water is formed, an anhydrous powder of a flea-brown colour is produced. It detonates powerfully when heated, or struck: the acids decompose it, forming salts of ammonium and mercury. If artificially cooled and made under pressure, according to Weyl, its composition is  $2\text{HgO}, \text{H}_2\text{N}$ . It is yellow if prepared in the dark, and is then soluble in hydrochloric acid. Water converts it at once into a white powder. If heated in a current of ammoniacal gas, water escapes and a dark powerfully explosive compound ( $\text{Hg}_2\text{N}$ ),  $\text{O}$  is obtained, possibly identical with Plantamour's compound: this compound becomes decomposed with evolution of ammonia on exposure to a moist atmosphere.

(927) *Mercuric sulphate, or Sulphate of mercury* ( $\text{HgSO}_4 = 296$ ); *Sp. Gr.* 6.466.—When 2 parts of mercury are heated gently with 3 of oil of vitriol, sulphurous anhydride is evolved, and mercurous sulphate is procured; but if the heat be increased, and the distillation be carried to dryness, mercuric sulphate is formed; sulphurous anhydride being extricated, whilst the mercury takes oxygen from the sulphuric acid;  $\text{Hg} + 2\text{H}_2\text{SO}_4 = \text{HgSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$ . It is a white crystalline powder, which is soluble in a solution of common salt, but is decomposed by pure water into an insoluble yellow basic salt, called *turpeth mineral* ( $\text{HgSO}_4, 2\text{HgO}$ ; *sp. gr.* 8.319), and a soluble acid salt, which crystallizes in deliquescent needles; the yellow basic salt is formed more rapidly if the sulphate be washed with boiling water. The normal sulphate, when treated with an excess of ammonia, yields mercuramine sulphate. The normal sulphate unites with ammoniac sulphate, with which it forms a crystallizable double salt.

(928) *NITRATES OF MERCURY*.—Mercury forms a larger number of nitrates than any other metal. The conditions of temperature, and dilution of acid necessary to ensure the production of each compound, often vary in each case but little, and their accurate analysis is attended with some difficulty. Different chemists vary somewhat in their statements of the results which they obtained. The *normal subnitrate*, or *mercurous nitrate* ( $\text{Hg}_2\text{NO}_3, 2\text{H}_2\text{O}$ ) is obtained by digesting metallic mercury in an excess of nitric acid diluted with 4 or 5 times its bulk of water; it crystallizes in short transparent somewhat efflorescent prisms

(or in rhombic plates; Gerhardt); water decomposes it into a yellow insoluble dibasic salt ( $\text{Hg}'_2\text{NO}_3, \text{Hg}_2\text{O}, \text{H}_2\text{O}$ ), or ( $2\text{Hg}_2\text{O}, \text{N}_2\text{O}_5, \text{H}_2\text{O}$ ), and a soluble acid one. A soluble subnitrate, which is often mistaken for the normal salt, crystallizes in large transparent colourless prisms [ $3(\text{Hg}'_2\text{NO}_3), \text{Hg}'_2\text{O}, \text{H}_2\text{O}$ ], or ( $4\text{Hg}_2\text{O}, 3\text{N}_2\text{O}_5, \text{H}_2\text{O}$ ), and is obtained by digesting an excess of mercury in diluted nitric acid. De Marignac finds that by boiling the mother-liquors of the preceding salts upon an excess of mercury for several hours, doubly oblique, rhombic, colourless prisms are deposited, to which he assigns the composition [ $3(\text{Hg}_2\text{NO}_3), 2(\text{Hg}'_2\text{O}, \text{H}_2\text{O})$ ], or ( $5\text{Hg}_2\text{O}, 3\text{N}_2\text{O}_5, 2\text{H}_2\text{O}$ ). Other subnitrates also appear to exist. These various basic nitrates may be distinguished from the normal salt by triturating them with sodic chloride, when they become grey, owing to the separation of black mercurous oxide, while calomel is formed; but the normal salt remains white.

A normal *mercuric nitrate* [ $2(\text{Hg}''\text{NO}_3), \text{H}_2\text{O}$ ] is slowly formed in voluminous crystals, by dissolving mercuric oxide in an excess of nitric acid, and evaporating the liquid until it assumes a syrupy consistence. Another nitrate ( $\text{Hg}_2\text{NO}_3, \text{HgO}, 2\text{H}_2\text{O}$ , or  $2\text{HgO}, \text{N}_2\text{O}_5, 2\text{H}_2\text{O}$ ) is deposited in acicular crystals from a boiling solution of mercury in excess of nitric acid; but it is obtained with greater certainty by saturating nitric acid, of sp. gr. 1.4, diluted with an equal bulk of water, with the mercuric oxide. The solutions of both these salts are decomposed when diluted freely with water, and a yellow insoluble basic nitrate ( $\text{Hg}_2\text{NO}_3, 2\text{HgO}, \text{H}_2\text{O}$ , or  $3\text{HgO}, \text{N}_2\text{O}_5, \text{H}_2\text{O}$ ) is precipitated: by long-continued washing with hot water, the whole of the nitric acid is removed from this basic salt, and mercuric oxide is left. Solutions of the mercuric nitrates, when digested upon an excess of the metal, are converted into mercurous nitrates.

(929) CHARACTERS OF THE SALTS OF MERCURY.—Most of the salts of mercury are colourless, but some of the basic mercuric salts are yellow. The following characters are common to both the mercurous and mercuric salts. The soluble compounds have an acrid, nauseous, metallic taste: in large doses they act as irritant poisons. All the mercurial compounds are volatilized by heat. If a small quantity of any of the dry salts of this metal be placed at the bottom of a tube of the diameter of a quill, and be covered to the depth of 1 inch ( $25^{\text{mm}}$ ) with a layer of dried sodic or potassic carbonate, mercury may be obtained in the form of a sublimate of minute globules, by heating the upper part of the

layer of the carbonate to redness, and driving the vapour of the mercurial compound slowly through it.

The presence of mercury, when in solution, may be detected by placing a small strip of zinc, round which a thin strip of gold foil is twisted, in a portion of the liquid to be tested. The mercury will be deposited by voltaic action in the form of a white stain upon the gold. This stain will disappear on heating the gold to redness. The salts of mercury, whether soluble or insoluble, are all reduced to the metallic state when heated with a solution of *stannous chloride*. A strip of metallic *copper* becomes coated with a white amalgam, if rubbed with a solution containing mercury. This test may be employed for detecting the presence of mercury in solution if applied by the method of Reinsch for arsenic (846), a sublimate of mercury in distinct globules being obtained by heating the coated slip in a small tube.

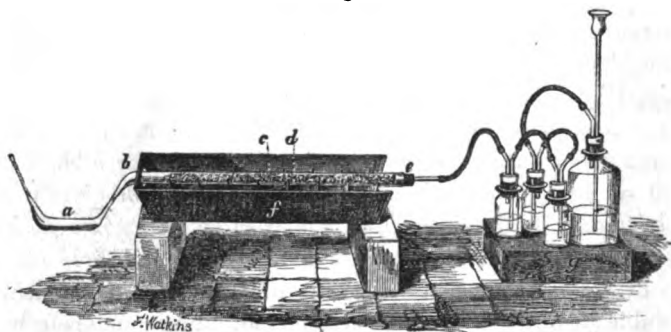
1.—*Mercurous salts* are characterized, when in solution, by yielding with solutions of *potash*, of *soda*, or of *lime*, a black precipitate of mercurous oxide. *Potassic ferrocyanide* gives a white precipitate. Both *sulphuretted hydrogen* and *ammonic hydrosulphide* yield a black mercurous sulphide. *Hydrochloric acid* and solutions of the *chlorides* cause a white precipitate of calomel, which is soluble in hot concentrated nitric acid, and in chlorine water; it is blackened by the addition of an excess of ammonia. *Potassic iodide* gives a green mercurous iodide, and *potassic chromate* a bright red basic mercurous chromate.

2.—*Mercuric salts*, when in solution, yield with solutions of *potash*, of *soda*, and of *lime*, a bright yellow precipitate of mercuric oxide; with *ammonia*, a white precipitate; with *normal potassic carbonate*, a yellow precipitate of oxide, with *potassic hydrocarbonate*, a red precipitate of mercuric oxychloride (923): all these precipitates are soluble in hydrochloric acid. *Ammonic hydrosulphide* gives a black precipitate; and *sulphuretted hydrogen*, a dirty white precipitate, which passes through red into black; it is insoluble in nitric or in hydrochloric acid: this sulphide is insoluble in the sulphides of the alkali-metals unless an excess of alkali be present, in which case the precipitate is gradually dissolved. *Potassic iodide* precipitates a salmon-coloured mercuric iodide, which quickly becomes of a brilliant scarlet: this precipitate is soluble in excess both of potassic iodide, and of corrosive sublimate. *Hydrochloric acid* and solutions of the *chlorides* give no precipitate with the mercuric salts. *Potassic ferrocyanide* gives a white precipitate, which gradually becomes blue, while mercuric cyanide is formed in the solution.

(930) *Estimation of Mercury*.—Mercury is usually estimated in the metallic form. If the solution contain neither lead nor silver, metallic mercury may be precipitated by the addition of stannous chloride, acidulated with hydrochloric acid: the metal must be collected on a weighed filter, and dried *in vacuo* over sulphuric acid.

When the compound is in the solid form, Millon recommends the following plan for effecting the decomposition of the combinations of mercury and for collecting the metal:—A hard glass tube, 18 or 20 inches (45 or 50<sup>cm.</sup>) long, such as is used in the analysis of organic compounds, is drawn out in the manner represented in fig. 366, and at *a* a small bulb is formed for the reception of the

FIG. 366.



mercury; a plug of asbestos is placed at *b*; the tube is then filled as far as *c* with fragments of quicklime, and the mercurial compound, in quantity varying from 15 to 45 grains (1 to 3 grammes), is introduced between *c* and *d*, and the tube is filled up with fragments of lime. If nitric acid be present in the compound, metallic copper must be substituted for quicklime. The extremity, *e*, is connected with an apparatus, *g*, which supplies a steady current of pure dry hydrogen,—the tube being placed in a sheet-iron furnace, *f*, while the receiver, *a*, projects beyond the furnace, and is kept cool. As soon as the apparatus is filled with the gas, lighted charcoal is applied to the first third of the tube between *b* and *c*, and when it is at a full red heat, glowing charcoal is very gradually added until the whole length of the tube is red hot; the mercury collects in *a*, and the water, which is at first condensed, is gradually removed by the current of dry hydrogen. When the operation is over, the narrow portion of the tube between *a* and *b* is cut with a file, and the detached portion *a*, with its contents, is weighed: the mercury is emptied, the bulb cleansed with nitric acid and water, then dried, and weighed a second time; the difference gives the weight of the condensed mercury.

§ II. SILVER: (Argentum)  $\text{Ag} = 108$ . *Sp. Gr.* 10.53;  
*Fusing-pt.* 1873° (1023° C.).

(931) SILVER has been known from the earliest ages, and has always been prized for its rarity, beauty, and its brilliant lustre. It has a white colour with a tinge of red; in hardness it is intermediate between copper and gold, and it is endowed with con-

siderable tenacity ; it may be hammered into very thin leaves, and admits of being drawn into very fine wire. By repeated heatings, however, this metal assumes a crystalline texture, and it then becomes brittle. It crystallizes in forms belonging to the regular system. Silver fuses at  $1873^{\circ}$  ( $1023^{\circ}$  C.), and on cooling expands forcibly at the moment of solidification. It is not sensibly volatilized if heated in closed vessels, but a silver wire is dispersed in greenish vapours when a very powerful electrical discharge is sent through it ; when heated before the oxyhydrogen jet on lime (966) it may be made to boil, and give off vapours which become oxidized in the current of gas if it contains an excess of oxygen.

In his elaborate researches upon the combining proportions of the elements, Stas has availed himself of the volatility of silver in the heat of the oxyhydrogen jet to obtain the metal in a state of absolute purity. For this purpose in a block of lime, from white marble, 25 or 30<sup>cm.</sup> long, 10<sup>cm.</sup> high, and as many in thickness, a cavity 3<sup>cm.</sup> in diameter and 2<sup>cm.</sup> deep was drilled ; and connected with a sloping channel of 3<sup>cm.</sup> wide and 5<sup>mm.</sup> deep, which acted as a condenser to the silver : the channel terminated in a cavity for the reception of the distilled metal. A cover of lime was fitted to this sort of still, and 50 grammes of silver were introduced into the cavity, heated by the oxyhydrogen jet ; in this way the whole of the silver was distilled in from 10 to 15 minutes, but a good deal escaped condensation.

Silver is an excellent conductor both of heat and electricity, and is not inferior in these respects to any known substance. Silver is not oxidized by exposure at any temperature either in a dry or a moist atmosphere. Pure silver, however, when melted, absorbs oxygen mechanically, to an extent amounting, it is said, to 22 times the bulk of the metal, but the gas is given off at the moment of solidification : if a mass of melted silver be allowed to cool suddenly, the outer crust becomes solidified, and when the interior portion assumes the solid condition it ruptures the crust ; small tubes or globules of melted metal are then forcibly expelled by the escaping oxygen, aided by the sudden expansion which the silver undergoes in the act of solidification. This phenomenon, which is termed the *spitting* of the globule, is entirely prevented by the presence of 1 or 2 per cent. of copper. Silver combines slowly with chlorine, with bromine, and with iodine : if fused with phosphorus the two bodies enter into combination. Silver has a powerful attraction for sulphur ; by long exposure to the air the metal becomes superficially blackened or tarnished, from the formation of a thin film of sulphide upon its surface, owing to the decomposing action of the metal upon the small portion of sulphuretted hydrogen which is constantly floating in the air, especially of large towns. This tarnish is readily removed by means of a solution of potassic cyanide.



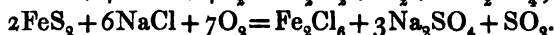
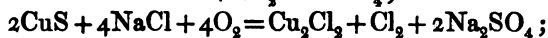
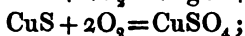
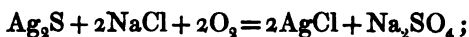
The best solvent for silver is nitric acid, which, if diluted with an equal bulk of water, acts upon the metal with great violence, dissolving it rapidly and evolving nitric oxide, while argentic nitrate is formed. Hydrochloric acid acts but slightly upon it. Aqua regia attacks it more rapidly. Diluted hydriodic acid attacks it with evolution of hydrogen. Boiling oil of vitriol dissolves it with evolution of sulphurous anhydride. If common salt be fused in a silver dish, or if it be moistened and left in contact with silver, it gradually corrodes it; soda being formed by the absorption of oxygen from the air, while the liberated chlorine attacks the silver. Neither the hydrated alkalies nor their nitrates exert any considerable action upon it, whether in solution or when fused by heat, and hence crucibles for the fusion of refractory minerals with caustic potash are commonly made of this metal.

The value of silver as a medium of exchange has caused it to be adopted as such by all civilized nations from the earliest ages of the world. When alloyed with certain proportions of copper it is used for the current coin of the realm, and for the various articles of plate. From its superior power of reflecting light, it forms the best surface for the reflectors employed in lighthouses at sea.

(932) *Extraction of Silver from its Ores.*—Silver is frequently met with in the native state; either pure, when it occurs in fibrous masses, or crystallized in cubes or octohedra; or sometimes combined with gold, mercury, or antimony: generally, however, it is found in combination with sulphur, mixed with sulphides of lead, antimony, copper, and iron. The mines of Peru and Mexico are the most extensive sources of silver. In Europe, those of Kongsberg in Norway, and of Schneeberg and Freyberg in Saxony, are celebrated: there are also numerous other mines from which smaller quantities are obtained. The ores of silver occur usually among the primitive rocks, frequently in calcareous veins, traversing either gneiss, or slaty and micaceous deposits. Plumbic sulphide is nearly always accompanied by small quantities of argentic sulphide, and a considerable quantity of silver is extracted during the refining of lead by Pattinson's process (891), as well as by cupellation (892).

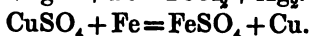
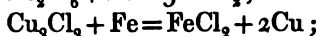
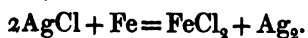
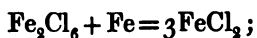
At Freyberg, silver is for the most part obtained from the sulphide by the method of *amalgamation*. The plumbiferous ores are in this case rejected, as they are not adapted to this method of proceeding, but are treated in the manner already described when speaking of lead. The ores are usually sorted, so that they shall contain about 0.24 parts of silver in 100, or about 80 ounces

per ton of ore, and not more than 1 per cent. of copper; the proportion of iron pyrites is not allowed to exceed, or greatly to fall short of 35 per cent. The metalliferous mass, after it has been reduced to a coarse powder, is mixed with a tenth of its weight of common salt, and sifted, to ensure its intimate incorporation: it is then roasted, at first at a low red heat; during this operation, care is taken to keep the mixture constantly stirred, in order as far as possible to prevent it from concreting into lumps. Meantime arsenic and antimony are expelled in dense white fumes of arsenious and antimonious sesquioxide, and the sulphides of the other metals are partially oxidized; the silver obtains chlorine from the salt, the sodium of which unites with oxygen and sulphur, argentic chloride and sodic sulphate being formed; the copper and the iron are changed partly into sulphates, partly into chlorides, and partly into oxides, as the equations subjoined will show:—



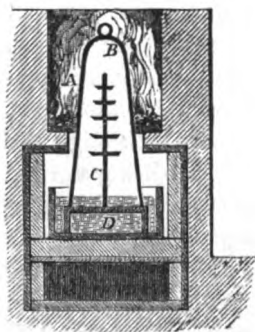
During the early stages of this operation, fumes of sulphurous anhydride are given off abundantly; and the roasting is continued until these have in great measure given place to those of chlorine and ferric chloride. A charge of  $4\frac{1}{2}$  cwt. requires 6 hours' roasting. The roasted mass is now raked out of the furnace, and allowed to cool: it is next sifted in order to separate the lumps, which are powdered and again submitted to the same operation. About 85 per cent. of the silver is thus converted into chloride at the first roasting. The portions which have passed through the sieve are ground to powder, and passed through a bolting sieve to procure a very fine meal. The powder is next placed, with from a third to half its weight of water, in large casks, which are charged with about 500 kilos., or half a ton of the ore. These casks are caused to revolve upon horizontal axes, about 20 times per minute; 50 kilos., or about 1 cwt. of scrap wrought iron is then introduced into each cask, and after the lapse of an hour, 250 kilos., or about 5 cwt. of mercury is added, after which the casks are again made to revolve for about 20 hours; during this operation a slight rise of temperature is observed. The powder when placed in the casks consists principally of argentic chloride mixed with large quantities of cupric sulphate and cupreous chloride, as well as of ferric chloride, with a variable proportion of the oxides of copper and iron. The object of agitating the mixture

with the iron before adding the mercury is to reduce the ferric chloride to ferrous chloride in the first instance; if this precaution were not taken, the mercury would be partially converted into calomel, which would not subsequently be decomposed, and would thus be lost: the excess of iron afterwards removes the chlorine from the argentic chloride and cupreous chloride, and the sulphuric acid from the copper:—



The presence of the mercury favours this reaction, by establishing a voltaic current, and the silver and copper thus set at liberty unite immediately with the mercury, forming a liquid amalgam. At the expiration of 18 or 20 hours the casks are filled up with water, and are again set in motion for a couple of hours to allow the amalgam to be washed out of the spent materials; after which the fluid amalgam is drawn off into sacks of ticking; these sacks form a kind of rude filter, through which the greater part of the mercury runs into a stone trough, leaving behind it a soft solid containing from 15 to 17 per cent. of silver. The mud in the casks is again submitted to washing; the residual amalgam subsides, owing to its greater density, and the lighter portions are rejected. The filtered part of the mercury, which retains a small

FIG. 367.



quantity of silver, is used again for the amalgamation of a fresh portion of ore. The silver in the solid amalgam has now to be separated from the remaining mercury; for this purpose it is placed in trays, supported on a tripod, c, fig. 367, under a large distillatory iron bell, B, round the upper part of which a fire, A, is lighted; the bell and its contents are thus brought to a red heat, by which means the mercury is driven off; its vapour descends, and is condensed in the water contained in the vessel, D. The operation is generally

performed on 250 kilos., or about 5 cwt. of amalgam at a time, and occupies 8 hours. The residual spongy mass of silver and copper is then fused and cast into ingots, which in the Saxon mines contain usually about 70 per cent. of pure silver and 28 of copper.

An improvement upon this process has been introduced by Augustin, who dispenses with the use of mercury altogether. After the ore has been roasted first by itself, and again a second time with sodic chloride, it is digested in a

concentrated solution of common salt;—such a solution dissolves argentic chloride readily: a dilute solution of sodic chloride exerts little or no solvent action; and the concentrated liquid when diluted deposits the argentic chloride which it had previously dissolved. In practice it is found better, instead of diluting the liquid, to digest it upon metallic copper; the chloride of silver is decomposed, chloride of copper is formed and dissolved, whilst metallic silver is precipitated. The presence of cupric chloride in the solution of the sodic chloride does not prevent the liquid from being employed again for the extraction of chloride of silver from fresh portions of the roasted ore.

Another important improvement in the operation was made by Zivvogel. He avoids the preparation of argentic chloride entirely, and merely roasts the sulphurous ores in such a manner that the sulphates of iron and copper are completely decomposed, whilst the argentic sulphate, which withstands a much higher temperature, remains undecomposed in the mass. In this operation the powdered ore is roasted till it gives off no odour of sulphurous anhydride, and yields no sensible amount of cupric sulphate when thrown red hot into water: boiling water then dissolves out the argentic sulphate, but the oxides of copper and iron remain undissolved. The silver is precipitated from the liquid by means of metallic copper as before. A small quantity of silver is still retained in the undissolved residue, from which it may be advantageously extracted by the method of Augustin. Both these processes have been patented and practised on a large scale in England.

Percy has suggested the use of sodic hyposulphite as a solvent for argentic chloride. The mineral after roasting with sodic chloride is washed first with hot and then with cold water, and afterwards is digested in a dilute solution of the alkaline hyposulphite, which dissolves the argentic chloride; from this solution the silver is precipitated as sulphide, by means of sodic sulphide, whilst sodic hyposulphite is reproduced as before.

(933) *American Process of Amalgamation.*—In the mining districts of Mexico and Chili, where fuel is expensive, and where ores are often worked of a much poorer description than in Europe, the process of amalgamation is different. A good deal of the silver occurs in the native state, so that it unites directly with the mercury. The mineral is stamped and ground to a fine powder in mills, then moistened with water, and mingled with from 1 to 5 per cent. of salt; the mixing is effected by the trampling of horses during 6 or 8 hours. The ore thus blended with the salt is allowed to remain undisturbed for some days, after which an addition of  $\frac{1}{800}$  or  $\frac{1}{1000}$  of its weight of what is technically termed *magistral* is made. This substance consists of roasted copper pyrites, and contains about 10 per cent. of cupric sulphate, the remainder being ferrous sulphate and other impurities; mercury, to the extent of twice the quantity of silver that the ore contains, is then added, the mixture being effected, as before, by the trampling of horses. It is again allowed to rest for 16 or 20 days: during this period a considerable portion of the silver becomes united with the mercury, forming a hard, brilliant amalgam, and at the same time a large quantity of calomel is formed.

Another equal quantity of mercury is added, and a still longer interval of rest is allowed; then a third dose of mercury to the same extent follows; by this last addition a fluid amalgam is obtained, which is separated by washing, filtered, and the mercury is expelled from the silver by distillation. The quantity of mercury consumed in this process varies from 130 to 150 parts for each 100 parts of silver extracted, great waste being incurred owing to the formation of calomel, which is not recovered. It is calculated that up to the close of the last century, 6 million cwt. of mercury had thus been lost by the processes adopted in the American mines in the course of 200 years.\*

The theory of this operation is rather obscure. The cupric sulphate of the magistral, and the sodic chloride decompose each other, cupric chloride and sodic sulphate being formed. Cupric chloride, in the presence of metallic silver, is converted into cupreous chloride, whilst argentic chloride is produced;  $2\text{Cu}''\text{Cl}_2 + \text{Ag} = \text{Cu}'_2\text{Cl}_2 + 2\text{AgCl}$ . When cupreous chloride, with excess of common salt and water, is brought into contact with argentic sulphide, the cupreous chloride is dissolved by the solution of sodic chloride; this solution of cupreous chloride decomposes the argentic sulphide, and is converted into cupreous sulphide, whilst argentic chloride is formed;  $\text{Cu}'_2\text{Cl}_2 + \text{Ag}_2\text{S} = \text{Cu}'_2\text{S} + 2\text{AgCl}$ . The excess of salt dissolves the argentic chloride, and the addition of mercury decomposes this dissolved chloride; calomel is formed, and an amalgam of silver is procured;  $2\text{AgCl} + 2\text{Hg} = 2\text{HgCl} + \text{Ag}_2$ . If too much magistral be added, an excess of cupric chloride ( $\text{CuCl}_2$ ) is produced; this state of the mixture is easily perceived, for in such a case the globules of mercury in the mixture appear to be too minutely divided; the addition of lime then becomes necessary in order to decompose the excess of the cupric chloride, otherwise this salt would reconvert the silver into chloride, and the mercury into calomel.

(934) *Separation of Silver from Copper by Liquation.*—It occasionally happens that a copper ore contains a considerable amount of silver, which, under certain circumstances, it may be desirable to extract by the process of *liquation*. For this purpose the copper, having been brought to the stage of blister copper (870), is melted with from 3 to 4 times its weight of lead: the mixture is cast

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\* Dumas proposes to recover this mercury by treating the washed residue with a quantity of chloride of lime or sodic nitrate, proportioned to the mercury they contain, then adding hydrochloric acid in slight excess; the calomel would thus be converted into corrosive sublimate. This is to be removed by methodical washing, and the mercury precipitated by copper. The solution of copper thus obtained would furnish the magistral required for a new operation upon fresh ore

into circular ingots in iron moulds, which suddenly cool the alloy, and cause it to solidify before the copper and lead have time to separate from each other. The proportion of lead should not be less than 500 times that of the silver in the mass. These cakes are then subjected to the action of a moderate heat; the lead, combined with nearly all the silver, and a small proportion only of copper, gradually runs from the mass, leaving a spongy residue, consisting chiefly of copper, but still retaining a small proportion of lead. The argentiferous lead is afterwards subjected to the process of cupellation, whilst the copper from which it has been separated is subjected to a patient roasting in order to oxidize the remainder of the lead, and it is then refined much in the usual manner.

(935) *Plating and Silvering*.—Silver is frequently employed to give a coating to the surface of less expensive metals. Goods so prepared are said to be *plated*, if the proportion of silver be considerable, and *silvered* if it be small. Plating on copper is effected by polishing the upper surface of the ingot which is to be plated, and then placing upon it a bright slip of silver, the superficial area of which is a little smaller than that of the copper which it is intended to cover: the thickness of the plate of silver in proportion to that of the copper varies with the value of the goods. The compound ingot is then exposed to a temperature just below the fusing-point of the silver, which softens at its surface. By hammering or rolling out at this high heat, the two metals are *sweated* together, as it is termed, and become inseparably united. No solder is used in this process, but a small portion of powdered borax is placed round the edge of the silver to prevent the surface of the copper from becoming oxidated. The ingot is then rolled until it is reduced to the required degree of tenuity.

Plating on steel is effected rather differently. The article (a dessert knife, for example) having been first brought to the shape required, is tinned upon its surface, and then a slip of silver foil is soldered on. After the silver has been attached, the superfluous portion is removed, and the article is finished up and polished.

These methods of plating have, however, been in a great degree superseded by the process of electro-plating, in which the silver is deposited upon the surface by voltaic action (295).

Silvering may be effected either by the *wet* or by the *dry* method. The wet method is usually adopted for such purposes as the silvering of thermometer scales. It is generally executed either on brass or on copper: the surface of these metals is cleaned by *dipping*, or momentary immersion of the articles in nitric acid, to remove the film of oxide which always forms from exposure to the atmosphere, even for a few hours. After rinsing them in water to remove the nitric acid, they are rubbed over

with a mixture of 100 parts of cream of tartar, 10 of argentic chloride, and 1 part of corrosive sublimate. The mercury appears to act as a kind of solder to the silver, the copper combining with the chlorine both of the chloride of silver and of the sublimate; the surface is afterwards polished.

Dry silvering is effected by dissolving a certain quantity of silver in mercury; the 'dipped' articles are agitated with a portion of this amalgam, which thus becomes diffused uniformly over the surface. By the application of heat the mercury is expelled, leaving a very thin film of silver behind: on polishing the trinkets a bright silvered surface is obtained.

(936) *Silvering of Mirrors*.—Some of the salts of silver when rendered slightly ammoniacal and mixed with certain organic solutions, such as aldehyd or grape-sugar, are reduced to the metallic state, the silver being deposited upon the surfaces of glass vessels in which the experiment is made, in the form of a brilliant, adhering, mirror-like coating. Mr. Drayton some years ago proposed to apply this observation to the silvering of mirrors upon a large scale, as the coating adapts itself not only to flat surfaces, but to those also which are curved, or cut into patterns. This process is now successfully practised in Paris, as follows:—40 grms. of pure neutral argentic nitrate are dissolved in 80 c. c. of water. To this solution are added: 1st, 5 c. c. of a liquor prepared from 25 parts of distilled water, 10 of ammoniac sesquicarbonate, and 10 of a solution of ammonia of sp. gr. 0.980; 2nd, 2 c. c. of a solution of ammonia of sp. gr. 0.980; and 3rd, 120 grms. of alcohol of sp. gr. 0.850. The mixture is left at rest to become clear. The liquid is decanted or filtered, and a mixture of equal parts of alcohol (sp. gr. 0.850) and oil of cassia is added in the proportion of 1 part of this *essence of cassia* to 15 parts of the solution of silver; the mixture is agitated and left to settle for several hours, after which it is filtered. Just before pouring it upon the glass to be silvered, it is mixed with  $\frac{1}{8}$  of its bulk of *essence of cloves* (composed of 1 part of oil of cloves, and 3 of alcohol, sp. gr. 0.850). The glass, having been thoroughly cleansed, is covered with the silvering liquid, and warmed to about 104° (40° C.), at which temperature it is maintained for two or three hours: the liquid is then decanted, and may be employed for silvering other glasses. The deposit of silver upon the glass is washed, dried, and then varnished. (Pelouze and Fremy, *Traité de Chimie*, 2nd ed., iii. 347).

An alcoholic solution of grape-sugar produces the same result, if substituted for the oils of cassia and cloves, but the deposit occurs much more slowly. Liebig's method of reducing an ammoniacal solution of argentic nitrate alkalized with soda or potash, by means of milk-sugar, at ordinary temperatures, has been successfully applied by Steinheil, in the following manner, to the silvering of mirrors for telescopes (*Liebig's Annal.* xviii. 132):—Dissolve in 200 measures of water  $\frac{1}{10}$  of their weight of pure argentic nitrate, and add to the liquid a solution of caustic ammonia in quantity just sufficient to redissolve the argentic oxide which is at first precipitated; add to this solution 450 measures of a solution of caustic soda (of sp. gr. 1.035) free from chloride, and immediately redissolve the dark-brown precipitate thus produced, by the cautious addition of caustic ammonia, after which dilute the liquid with water to 1450 measures; then add a solution of argentic nitrate till a decided permanent grey precipitate is formed, and finally pour in water till the mixture occupies exactly 1500 measures: then leave it to stand, and decant the clear liquid. Immediately before the solution is to be used, it is to be mixed with an eighth or a tenth of its

volume of a solution of milk-sugar in ten times its weight of water. The solution is to be placed in a shallow vessel, and the glass to be silvered supported just at the surface of the liquid: a beautiful coherent film of silver is deposited upon the under surface of the glass, and a copious precipitation of silver occurs upon the sides of the vessel.

Another very good method of silvering glass is that of Petit-Jean (*Chem. Gaz.*, 1856, p. 319), in which an ammoniacal solution of tartrate of silver is employed at a gentle heat; by using a solution of auric ammonio-citrate, it is easy to gild upon glass; and in a similar manner the surface may be platinized if a solution of sodio-platinic tartrate be employed.

(937) *Alloys of Silver*.—Various alloys of silver may be obtained with facility, but the only one extensively used is the alloy of silver with copper. Pure silver is too soft for ordinary uses, such as the fabrication of coin, and jeweller's work, and would soon waste by the constant friction it would experience. In order to confer a sufficient degree of hardness upon the silver, it is combined with a small quantity of copper. The proportion of copper in the 'standard' silver employed for coinage varies in different countries: in England it amounts to 7.5 per cent., in France to 10 per cent., and in Prussia to 25 per cent. English standard silver has a density of 10.30.

Experience has shown that an alloy of silver and copper, however carefully the two metals be incorporated, undergoes a species of liquation during the slow solidification of the melted mass: when cast into ingots, the interior parts of the bars have a composition different from that of the superficial portions,—a circumstance of some importance in the preparation of standard silver for the purposes of coinage. The only alloy in which this partial separation of the two metals was found not to occur is stated by Levol (*Ann. de Chimie*, III. xxxvi. 220), to consist of 719 parts of silver and 281 of copper, corresponding to the formula  $\text{Ag}_7\text{Cu}_{28}$ . This liquation is comparatively trifling in amount in bars which contain 950 parts of silver and upwards in 1000: in bars which contain a larger proportion of silver than 719 in 1000 of alloy, the central portions of the ingot were found to be richer than those upon the surface; but in the alloys of lower value the proportion of silver was greatest on the surface of the ingot.

Silver, when alloyed with many of the metals in small quantity, is rendered brittle and unfit for the purposes of coinage. This is the case, for instance, when the silver contains tin, zinc, antimony, bismuth, lead, or arsenicum. These metals are, however, all easily removed in the ordinary course of refining. The alloy used as a *solder* for silver consists of 6 parts of brass, 5 of silver, and 2 of zinc. Silver appears to have the power of dissolving its sulphide: a quantity of sulphide not exceeding 1 per cent. renders the mass so brittle that it cannot be rolled.

(938) *Assay of Silver by Cupellation*.—From the high price of silver, compared with that of the metals used to harden it, it has become an object of great importance to be able to determine with facility and with accuracy the proportion of silver in any compound.



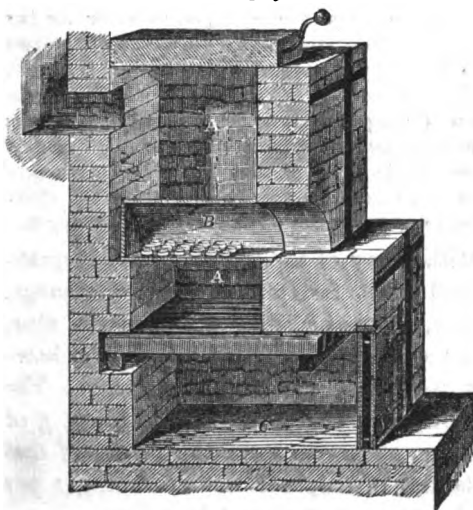
Jeweller's silver must according to law be of a certain degree of fineness. In this country each article, previously to being sold, is tested at Goldsmith's Hall, and if approved is stamped. The method of testing commonly employed is termed *assaying* or *cupellation*. In principle it depends upon the property possessed by lead of absorbing oxygen at a high temperature, and of forming with it an easily fusible oxide, which imparts oxygen with facility to all those metals which yield oxides not reducible by heat alone. Most of the oxides\* thus formed unite with plumbic oxide, and produce a fusible glass which is easily absorbed by a porous crucible made of burnt bones, termed a *cupel*; whilst any silver that the mixture contains is left behind in a bright globule, which admits of being accurately weighed. The cupel and its contents

FIG. 368.



are shown in section in fig. 368. These cupels are prepared from bone ash (burnt to whiteness, and ground to a fine powder), by moistening it with water: a suitable quantity of the mixture is placed in a mould, and the required form and coherence are given to it by the blow of a mallet or of a press: the cupels are allowed to dry thoroughly before they are used. The assay may be conducted upon 1 gramme of silver.

FIG. 369.



The plan of proceeding is as follows:—In a convenient furnace, such as is shown in section at A A, fig. 369, is placed an earthenware oven or muffle, B, of semi-cylindrical form, closed at one end, and open at the other, with slits in the sides to allow the free circulation of the air: upon the floor of the muffle, a number of cupels are arranged in rows, and the temperature is raised to bright redness. Equal portions of the various samples of silver to be assayed are in the meantime accurately weighed, and wrapped in a quantity of pure thin sheet-lead, the weight of which varies with the purity of the alloy; the larger the

proportion of foreign metals that it contains, the greater is the quantity of lead

\* Oxides of tin, zinc, nickel, and iron, do not form a fusible combination with litharge, and the alloys which these metals yield with silver are consequently not adapted for cupellation.

needed. Each piece for assay is now placed in its allotted cupel, by means of a long pair of tongs. It fuses quickly; fumes of plumbic oxide are seen rising from the cupels, but the greater part of the oxide is absorbed by the cupel, and the silver is left behind in a state of purity. At the moment that the last portion of lead undergoes oxidation, the surface of the silver flashes, or lightens as it is technically termed, owing to the cause already explained (892). This phenomenon indicates that the process is completed. The button is allowed to cool very gradually, to prevent the loss of silver by dispersion from *spitting* (931); it is then detached from the cupel, brushed, and accurately weighed. If the piece of alloy originally taken weighed 1 gramme, the weight of the button in milligrammes gives the number of parts of silver in 1000 parts of alloy. A minute quantity of silver always passes into the cupel during the process, for which an allowance must be made in weighing the button; and if the proportion of lead be too great this loss is increased, but if too little be used, part of the copper is left in the bead. Upon an alloy which contains 925 parts of silver to 75 of copper, the loss is about 4 per 1000; and upon silver which contains 900 parts in 1000, the loss on the button is about 5 parts in 1000. In order to be able to estimate the amount of this loss in each operation, the best plan is to pass three or four *proofs* with each set of assays. These proofs consist of pieces of fine silver of known weight, which are mixed with quantities of lead and copper, approximatively of the same amount as those present in the assays under trial. The loss experienced by these proofs affords a method of checking the results of the assay. The amount of this loss varies with the temperature.

The most convenient system of reporting the fineness of silver is the decimal method, which is employed in most countries with the exception of England. The practice of reporting both gold and silver decimally was introduced a few years ago by Sir J. Herschel into the Mint of this country, and it probably will gradually supersede the cumbrous and artificial method which is still generally employed by the English assayers. Upon the decimal system, fine silver is termed 1000·0, and the report upon any sample of alloy simply indicates the number of parts of pure silver in 1000 which it contains. Thus English standard silver contains 925 parts of silver, and 75 of copper in 1000 of the alloy. French standard contains 900 parts of silver, and 100 of copper in 1000 of alloy. English standard would therefore be reported as 925; French standard as 900.

The proportions of lead which are generally employed for the cupellation of different alloys are the following:—

If 1000 parts of the alloy contain			It will require of lead	
1000 parts of fine silver			half its weight.	
950	"	...	...	3 times its weight.
925	"	...	...	5½ "
900	"	...	...	7 "
850	"	...	...	9 "
800	"	...	...	10 "
700	"	...	...	12 "
600	"	...	...	14 "
500, or less	"	...	...	16 or 17 "

A skilful assayer will generally be able at once to determine the comparative fineness of an article from its mere appearance, and will judge accordingly of the proportion of lead which it will require. Great care is needful in regulating the temperature of the furnace during the cupellation; if too high, a part of the silver will be lost by volatilization; if too low, portions of lead and copper are

liable to be retained. When the assay is properly performed, the button is brilliant, well rounded, free from irregularities, and somewhat granular upon its surface: it is readily detached from the cupel. If the assay adheres strongly to the cupel, or is irregular in its outline, it retains a portion of the alloy.

(939) *Assay of Silver by the Humid Process.*—The results of the process of the assay by cupellation, even in experienced hands, may vary as much as 2 parts in 1000: this circumstance induced Gay-Lussac to contrive a different method, which is now adopted not only in the French Mint, but is employed in the Mints of Great Britain and the United States, as well as in almost all the Mints of Europe: it admits of an accurate estimate of the value of an alloy to within 0.5 in 1000. This process depends upon the solution of the alloy in nitric acid, the precipitation of the silver from the nitrate in the form of an insoluble chloride, and the measurement of the amount of a standard solution of sodic chloride which is required to effect the complete precipitation of the silver in a given weight of the alloy. Argentic chloride easily collects into dense flocculi by agitation in a solution which is acidulated with nitric acid, and which contains no excess of soluble chlorides; so that the exact point at which the precipitate ceases to be formed is readily perceived.

A solution of common salt is prepared of such a strength that 100 grammes of it are exactly sufficient to precipitate 1 grm. of pure silver. 1 grm. of the alloy for examination is placed in a stoppered bottle capable of holding about 200 c. c., or 7 oz. of water, and by the aid of a gentle heat, is dissolved in 8 c. c. of nitric acid of specific gravity 1.25: the solution of salt is then

FIG. 370.

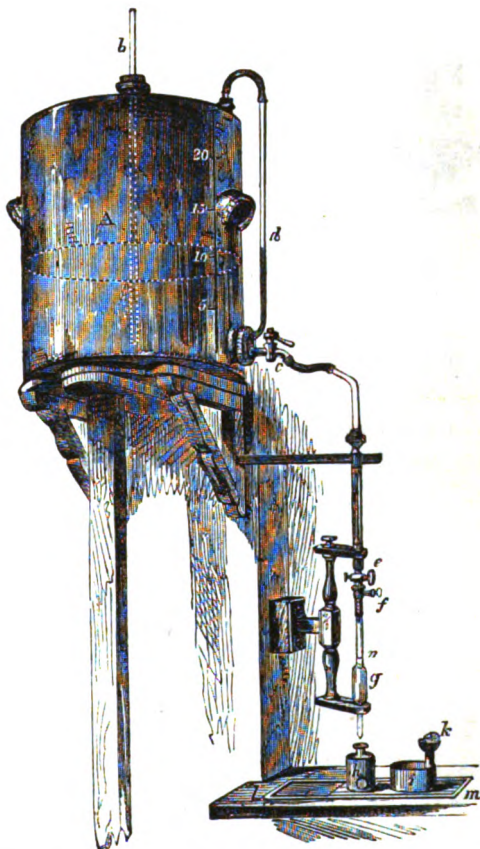


placed in a burette (fig. 370) capable of holding rather more than 100 c. c. The burette, when filled with the solution, is weighed before being used, and the liquid is added to the argentic nitrate in the bottle; when it is supposed that the silver is nearly all precipitated, the liquor is briskly agitated in the bottle, and the precipitate is allowed to subside; a drop or two more of the solution of salt is then added: if a precipitate be produced, the liquid is again agitated; and when clear, more of the solution is added, as before, so long as any turbidity is produced by the addition. When a cloud ceases to be formed, the proportion of solution of salt which has been added is ascertained by weighing the burette a second time. The number of decigrammes of the

solution employed indicates the degree of fineness of the alloy in thousandths.\*

When, as in the assay of bars for coin or for jeweller's work, a large number of assays must be executed, all very nearly of uniform fineness, the operation may be reduced to a system by which its precision may be increased, at the same time that it is rendered much more easy of execution. For this purpose, two solutions of salt are employed: one, the *standard solution*, containing in 100 c.c. a sufficient quantity of commercial sodic chloride to precipitate 1 grm. of silver;† the second solution, the *decimal solution*, having one-tenth of the strength of the first, and being prepared by diluting 1 litre of the standard solution with 9 litres of water. These solutions are to be preserved in well-closed bottles. The standard solution is prepared in large quantities at a time, and kept in stoneware jars, A, fig. 371, capable of containing from 90 to 125 litres (20 or 25 gallons): *b* is a tube open at both ends, which passes nearly to the bottom of the

FIG. 371.



jar, to admit air, whilst the liquid is drawn off by the stopcock, *c*, without allowing any loss by evaporation; *d* is a gauge by which the quantity of liquid within is indicated. A series of bottles, capable of containing about 200 c.c. (7 ounces) each, is fitted with ground stoppers, numbered consecutively from 1 upwards:

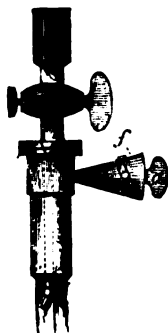
\* In the Calcutta Mint this precipitate is washed by subsidence in the vessel in which it is formed, and is then collected in a small porcelain crucible, as in the process of collecting gold, in the operation of *parting* (958). The chloride is dried, and then weighed, and the corresponding value of the silver is calculated.

† This solution contains approximately 5.416 grms. of sodic chloride per litre: but as the commercial salt contains magnesian chloride, the exact strength must be determined by dissolving a gramme of fine silver in acid, and precipitating it by the addition of 100 c.c. of the solution, ascertaining the amount of the excess or deficiency of chloride in the manner about to be detailed, and then adding water or salt as may be needed.

into each bottle 1 grm. of the alloy for assay is weighed; 8 c. c. of nitric acid are added to each bottle, which is placed in a shallow vessel containing water, and gradually raised to the boiling-point; in ten minutes the alloy is completely dissolved.

The precipitation of the silver in the form of chloride is then effected by the aid of the apparatus now to be described:—*g*, fig. 371, is a glass pipette which can be filled with the standard solution.

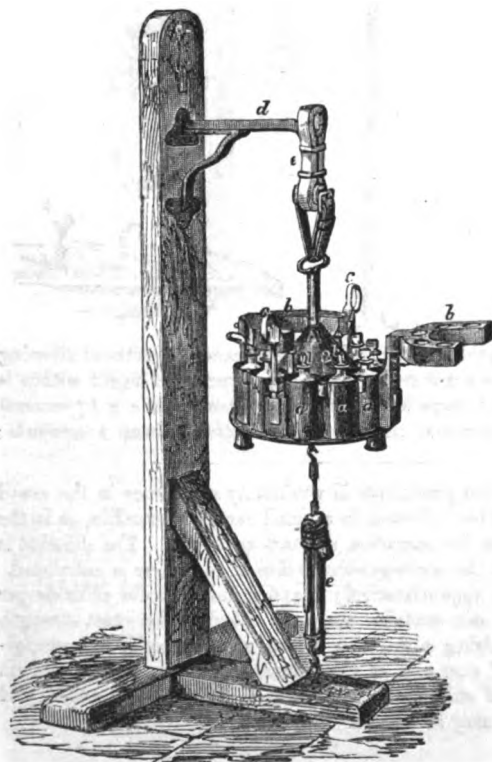
FIG. 372.



The quantity of liquid introduced into the pipette is regulated by means of the stopcock, *e* *f*, the peculiar construction of which is shown on a larger scale in fig. 372, in which *e* represents an ordinary stopcock (constructed of silver to resist the action of the solution), terminating below in a long tube, *c*; at *f* is an opening for the escape of air, which can be closed at pleasure by the plug, *a*. Suppose it be desired to fill the pipette, *g*, fig. 371; the lower opening of the pipette is closed by the forefinger, the solution is admitted by opening the stopcock, *e*, whilst the air escapes at *f*, which is open; as soon as the liquid has risen a little above the mark, *n*, both the stopcock, *e*, and the plug at *f*, are closed, and the finger is withdrawn. In this position the pipette will retain its charge for an indefinite time. The apparatus represented

at *m* *l* is intended to facilitate the exact emptying of the pipette; the tray, *k* *i*, slides easily between two grooves, in which its motion is limited by the

FIG. 373.



stops *l* and *m*; *k* is a compartment for the reception of the assay bottle, so adjusted that when the tray rests against the stop *m*, the pipette shall empty itself into the bottle without wetting its neck; *i* is another compartment for receiving the superfluous solution of salt, and *k* represents a piece of sponge, the object of which is to remove the drop which hangs to the lower end of the pipette; the stop *l* is so placed, that when the slide rests against it, the sponge shall just touch the lower extremity of the pipette. The sponge, *k*, having been brought to touch the lower end of the pipette, the plug at *f* is slightly relaxed to allow the air to enter, and a portion of the liquid gradually to escape, until it has fallen exactly to the mark *n*. The slide is now moved until the bottle, *k*, is directly underneath the pi-

pette, and on opening the plug at *f* to its full extent, the charge flows freely into the bottle.

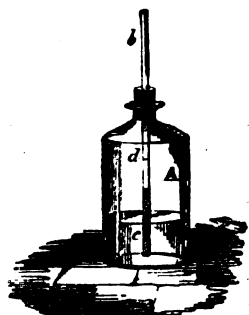
Suppose now the object of the assay be to ascertain whether a certain number of bars be of the fineness of English standard silver, or if not, what is the amount of their variation from standard. The pipette, *g*, is so graduated that when filled up to the mark *n*, it shall deliver exactly 92.2 c. c. of the standard solution, which will contain a sufficient amount of common salt to precipitate 0.922 gramme of silver; a quantity which is purposely rather less than the assay is expected to contain; 1 gramme of alloy, if of correct composition, containing 0.925 grm. of silver. When each bottle in succession has received from the pipette a charge of exactly the same value, the bottles are transferred to the *agitator*, shown at fig. 373, which is suspended from an iron arm, *d*, between two strong springs, *e*, *e*, made of vulcanized caoutchouc. This agitator is usually constructed to contain 10 bottles, which are lodged in the compartments, *a*, *a*; the stoppers are secured in their places by the rims, *b*, *b*, one of which is represented in the figure as thrown back for the admission of the bottles; the rims when closed are confined by the springs shown at *c*, *c*. On agitating the apparatus briskly for 60 or 80 seconds, the solutions become clear, and the bottles are removed from the agitator, and transferred to a stand, behind which is a black board divided into 10 numbered compartments, each bottle being placed opposite the compartment which corresponds with its number.

The adjustment of the remaining portion of the assay is made by means of the *decimal solution*. This is contained in a small bottle of from 284 to 340 c. c. (10 or 12 ounces) in capacity, fig. 374, provided with a tube or small pipette, *b*, open at both ends, but drawn out to a narrow aperture below. On this small pipette a mark, *c*, is made at a height corresponding exactly to 1 c. c. of the liquid, 1 c. c. of this solution containing sufficient chlorine to precipitate 1 milligramme of silver.

The assayer now plunges this small pipette into the decimal solution, and closing the upper opening of the tube with his forefinger, partially withdraws it from the bottle, and allows the liquid to escape until it stands exactly at the line of the graduation, *c*; he then transfers the pipette to the first bottle, and allows the solution to flow into it. The same operation is repeated with each assay bottle in succession. A mark is next made with a piece of chalk, opposite to each bottle in which a precipitate is occasioned. These bottles are then replaced in the agitator and shaken a second time; the solutions having thus again been rendered clear, are replaced upon the table, and a second pipette of the decimal solution is added to each of the bottles in which a precipitate was first produced. This operation is repeated until in each bottle no further precipitate is occasioned. The contents of the pipette, *g*, of the standard solution, which have been added to each assay, occasion a precipitate out of the 1 grm. equal to 0.922, or of 922 parts out of 1000 parts of alloy. Each pipette of decimal solution is equivalent to  $\frac{1}{1000}$  of fine silver in the alloy, and by counting the number of marks against each bottle, reckoning the last only as equal to half a thousandth, since a portion of it probably remains in the liquid in excess, the assayer ascertains the value of each bar. If, for instance, two marks stand opposite to any bottle, the fineness of the bar will be more than 923, but less than 924, and may be reported as 923.5.

But suppose that there be some bottles in which the addition of the first

FIG. 374.



pipette of the decimal solution produces no precipitate; these samples must be either exactly of the fineness 922, or below that point. The following method is adopted for completing the assay of these samples: a *decimal solution of silver* is prepared by dissolving 1 gramme of pure silver in nitric acid, and diluting it with distilled water till the solution occupies the bulk of 1000 c. c. of water; each cub. centim. of this liquid will then contain exactly 1 milligramme of silver. A bottle of this solution is provided with a pipette similar to that shown in fig. 374, but graduated to deliver 5 c. c. of the liquid from the mark *d*. Each of the assay bottles, which indicates a fineness below 922, is supplied with 5 c. c. of this decimal silver solution, or with 5 mgrms. of silver; a mark -5 is made upon the board against each of these bottles. The bottles are then agitated as before, and a fresh dose of 1 c. c. of the decimal *salt* solution is now added to each: if a cloud be thus produced, a mark is chalked against each bottle in which a precipitate is observed, and the bottles are again agitated, and another dose of decimal salt liquid is added, and so on, until a precipitate ceases to be formed. Suppose that the first two pipettes of the solution produce a cloud, but the third does not; each bottle, it will be remembered, received a dose of salt solution in the first instance, as usual, in addition to the quantity received after the decimal silver solution was added; the quantity of salt which has produced a precipitate is therefore equivalent to  $922 + 1 + 1\frac{1}{2}$ , or 924.5; but since 5 of silver have also been added beyond that which the alloy originally contained, the amount to be reported becomes  $924.5 - 5$ , or the fineness of the bar is 919.5. It is preferable, in cases where the bars are below the standard, to add an excess of silver solution at once, and then to estimate the excess of silver in the manner above described; because if, instead of acting thus, successive doses of 1 mgrm. of silver be added until no further precipitate is formed, it becomes very difficult to render the solution clear by agitation.

The standard solution of salt is prepared at a temperature, say, of  $15^{\circ}$  C., consequently the pipette, *g*, will only deliver a volume of liquid rigorously equal to 922 milligrammes of silver, at that temperature. At a higher temperature the liquid will expand, and a given volume will therefore contain a smaller amount of sodic chloride, whilst at a lower temperature it will contract, and will contain a larger amount. A correction for this variation in the strength of the liquid is therefore required. This is made very simply in the following manner:—Each time that a number of assays is made, a piece of fine silver, equal to 925 mgrms., is weighed off, dissolved in nitric acid, and assayed as above directed. The number of pipettes of the decimal solution of salt which is required to complete the precipitation is noted, and the value of the contents of the large pipette of standard solution, *g*, is thus verified upon each occasion. If, for example,  $2\frac{1}{2}$  pipettes of decimal solution were required for completing this precipitation, the large pipette would deliver a quantity of the solution sufficient to precipitate 922.5 mgrms. on that day, instead of 922. Any deviation from the calculated value is allowed for, and a correction is made upon the assays by means of a table constructed for the purpose.

It is easy to apply this apparatus to the assay of silver of other degrees of fineness; but it is necessary to know approximatively the value of the alloy, in order that a suitable weight of it may be dissolved in nitric acid. Suppose, for instance, a number of bars approximatively of the value of 900 (the French standard) are to be assayed: a piece of the alloy, which contains approximatively 925 mgrms. of fine silver, must be taken; the quantity required is easily calculated, since the weight of the alloy needed will be inversely as its fineness; for  $900 : 925 :: 1 \text{ grm.} : 1.0277 \text{ grm.}$  The weight required in this case will consequently be 1.0277 grm.

Mercury is the only metal the presence of which interferes with the accuracy

of the assay by the humid method; but the process may be modified so as to give correct results even in this case.

(940) *Preparation of Fine Silver*.—In order that the foregoing process shall be accurately performed, it is necessary to be provided with silver of absolute purity. The following is one of the best methods of procuring the metal in this condition. Standard silver is dissolved in nitric acid: the liquid is diluted, and decanted or filtered from undissolved particles of gold or of argentic sulphide, and the solution is precipitated by the addition of a solution of sodic chloride in slight excess. The precipitate is washed in a large jar by subsidence, until the washings are tasteless. The chloride is then mixed with oil of vitriol, in the proportion of 200 grms. to each kilog. of chloride, and several bars of zinc are placed in the mass; the zinc speedily becomes converted into zincic chloride, which is dissolved, whilst the silver is reduced to the metallic state, and by a voltaic action the reduction gradually extends through the mass;  $\text{Zn} + 2\text{AgCl} = \text{Ag}_2 + \text{ZnCl}_2$ . The mixture is not to be agitated. In the course of a day or two the decomposition is usually completed. If a portion of the reduced silver, after being thoroughly washed, is entirely soluble in nitric acid, the reduction is complete. The bars of zinc, with the crust which adheres to them, are then carefully removed, and the reduced metal is digested for two days with diluted sulphuric acid, to remove any portions of the basic salts of zinc which are occasionally formed, and is washed in a large vessel by subsidence, until the washings cease to precipitate argentic nitrate. The reduced silver may be dried, and cast into ingots if desired. The metal is refined in large quantities for commercial purposes in this manner. It is not absolutely pure, and therefore, for delicate chemical operations, it undergoes a further process of purification.

For this purpose it is redissolved in nitric acid, and a second time precipitated as chloride, pure hydrochloric acid being employed as the precipitant: the precipitated chloride is again washed by subsidence until the washings no longer redden litmus. The chloride of silver is next dried until it ceases to lose weight, 100 parts of the chloride are mixed with 70.4 of chalk, and 4.2 of powdered charcoal, and the mixture is heated in a deep clay crucible.\* The temperature is kept at a dull red heat for half an hour, after which it is gradually raised to full redness: a considerable disengagement of gas takes place, owing to the evolution of carbonic anhydride and carbonic oxide, and calcic oxychloride is formed, constituting a fusible slag, beneath which the pure silver collects;  $2\text{AgCl} + 2\text{CaCO}_3 + \text{C} = \text{CO} + 2\text{CO}_2 + \text{CaO}, \text{CaCl}_2 + \text{Ag}_2$ . The silver may be poured into an ingot mould, remelted in order to free it from slag, and afterwards rolled into

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\* The washed chloride may also be reduced without difficulty by fusion with about half its weight of dried sodic carbonate.



sheets. Silver sufficiently pure for all ordinary purposes may also be obtained in a crystalline form by boiling a slightly acid solution of nitrate or other salt of silver with sheet copper: the precipitated silver is well washed, digested in a solution of ammonia, to remove any traces of adhering cupric oxide, and again washed.

(941) **OXIDES OF SILVER.**—Silver forms three oxides; a sub-oxide,  $\text{Ag}_2\text{O}$ ; argentic oxide,  $\text{Ag}_2\text{O}$ , which is the basis of the salts of the metal; and a peroxide, probably  $\text{Ag}_2\text{O}_2$ , which does not combine with acids.

*Argentous oxide, or Suboxide of silver* ( $\text{Ag}_2\text{O}$ ).—According to Wöhler, if argentic citrate be heated to  $100^\circ\text{C}$ . in a current of hydrogen, the salt loses half an equivalent of oxygen, and a compound is produced which is sparingly soluble in water, forming with it a brown solution, from which, on the addition of potassic hydrate, a suboxide of silver is precipitated. This compound is very unstable; hydrochloric acid converts it partially into subchloride, but it is decomposed by other acids, and by ammonia, into argentic oxide and metallic silver. A mixture of metallic silver and argentous oxide is also obtained by boiling the yellow triargentic arsenite with a strong solution of caustic soda, trisodic arseniate being formed in the liquid,  $2\text{Ag}_3\text{AsO}_3 + 6\text{NaHO} = \text{Ag}_2\text{O} + \text{Ag}_2 + 2\text{Na}_3\text{AsO}_3 + 3\text{H}_2\text{O}$ .

*Argentic oxide, or Protoxide of silver* ( $\text{Ag}_2\text{O} = 232$ ; *Comp. in 100 parts*, Ag, 93.1; O, 6.9).—This oxide may be procured by adding a solution of potash or of soda to a solution of the nitrate or any soluble salt of silver. A brown hydrated oxide falls, which readily parts with its water, and if dried at a temperature above  $140^\circ$  ( $60^\circ\text{C}$ .), becomes anhydrous; it gives off oxygen below a red heat, and is reduced to the metallic state. Light also reduces it, and hydrogen, even at  $100^\circ\text{C}$ ., has a similar effect; contact under water with metallic tin or copper also deprives it of oxygen. Argentic oxide is a powerful base; it combines easily with acids, yielding salts which in some cases are isomorphous with the corresponding salts of sodium. They are almost always anhydrous. It forms with nitric acid a salt which is not acid in its reaction upon litmus. It is slightly soluble in pure water, to which it communicates a feebly alkaline reaction. Argentic oxide combines with the fusible silicates, and is sometimes employed for producing a yellow glass. Potassic and sodic hydrates do not dissolve the oxide, but it is freely soluble in ammonia, and the solution, by exposure to the air, deposits a black micaceous powder, which is powerfully explosive, and which has received the name of fulminating silver.

(942) *Fulminating silver* is also produced if a concentrated solution of ammonia be digested for some hours upon freshly precipitated argentic oxide; a black powder is formed which is allowed to dry in minute quantities on separate pieces of filtering paper. The same compound is formed on precipitating an ammoniacal solution of argentic nitrate or chloride by the addition of caustic potash. It is necessary to be aware of these facts, as it is a most dangerous

substance, and might be produced unintentionally. Friction or pressure, even when under water, occasions it to explode: and when dry, its detonation often occurs without any assignable cause. Acids immediately decompose it into an ammoniacal salt, and the corresponding salt of silver. The composition of this body, owing to its dangerous character, has not been accurately determined, but it is generally supposed to be a nitride, similar to that which is obtainable from mercury.

*Argentio peroxide* ( $\text{Ag}_2\text{O}_2$ ?) ; *Sp. Gr.* 5.474.—This compound is procured in dark grey acicular crystals, when a dilute solution of argentic nitrate is decomposed by means of the voltaic current. The peroxide accumulates upon the positive plate, but it always retains a certain quantity of undecomposed argentic nitrate. It is a conductor of the voltaic current. Acids decompose it, forming a salt of argentic oxide, whilst oxygen gas escapes. It is also decomposed by ammonia, with effervescence, owing to escape of nitrogen.

(943) ARGENTIC SULPHIDE, or *Sulphide of silver* ( $\text{Ag}_2\text{S}$  = 248) ; *Sp. Gr.* 7.2 ; *Comp. in 100 parts*, Ag, 87.1 ; S, 12.9.—This compound is the principal ore of silver. It is found native, sometimes crystallized in cubes or octohedra, at other times massive. It has a leaden-grey metallic lustre, from which it derives its mineralogical name of *silver glance*. Argentic sulphide is isomorphous with cupreous sulphide, and sometimes displaces it in certain minerals, such, for example, as polybasite, and fahlerz or grey copper ore (879).

Silver has a very powerful attraction for sulphur. The metal becomes tarnished, owing to the formation of a film of sulphide, if it be exposed to the action of sulphuretted hydrogen in the gaseous state, even though largely diluted with air ; and a black spot is immediately produced upon its surface by contact with a solution of a sulphide of one of the metals of the alkalis or alkaline earths. Argentic sulphide may be prepared by transmitting a current of sulphuretted hydrogen through solutions of the salts of silver, in which it forms a black precipitate ; or it may be obtained by heating silver with an excess of sulphur in a covered crucible ; in this case the argentic sulphide fuses, and forms a dark grey crystalline mass as it cools, and the excess of sulphur is volatilized.

Argentio sulphide is soft enough to allow of its being cut with a knife ; it also possesses sufficient malleability to receive impressions from a die. It is not a conductor of the voltaic current when cold, but if heated it transmits the current readily without undergoing decomposition. It is easily fusible, and if heated in closed vessels may be melted without becoming decom-

posed; but if roasted in the air, the sulphur is gradually converted into sulphurous anhydride, and metallic silver is left: during this operation a portion of it is usually converted into argentic sulphate, which afterwards requires an elevated temperature for its decomposition.

Argentic sulphide is decomposed when boiled with concentrated sulphuric acid, sulphurous anhydride and argentic sulphate being formed. Strong nitric acid also dissolves it by the aid of heat.\* Boiling hydrochloric acid converts it into argentic chloride, with evolution of sulphuretted hydrogen. Cupric chloride converts it into argentic chloride, with the formation of cupreous chloride and sulphide of copper: this change is much facilitated by the presence of sodic chloride in a moist state, as by its means both the argentic chloride and the cupreous chloride are dissolved at the moment of their formation. These reactions become important in the extraction of silver from its ores (932). Argentic sulphide is also decomposed when heated with the alkalis, and a similar effect is produced by igniting it with iron, copper, lead, and many other metals.

Argentic sulphide is not soluble in solutions of the sulphides of the alkali-metals; but it may be made to unite with many other metallic sulphides when fused with them. A native compound of this description is found in *red silver ore*, which is a double sulphide of silver and antimony,  $3\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$ . In this mineral a portion of antimonious sulphide is often displaced by arsenious sulphide.

(944) **CHLORIDES OF SILVER.**—There are two chlorides of silver, the subchloride,  $\text{Ag}_2\text{Cl}$ , and the protochloride,  $\text{AgCl}$ .

*Argentous chloride*, or *Subchloride of silver* ( $\text{Ag}_2\text{Cl}$ ) does not appear to have been obtained in a perfectly pure form. It is usually directed to be procured by digesting leaves of pure silver in a solution of cupric chloride or of ferric chloride; it forms black scales which are not acted upon by nitric acid, but are resolved by ammonia into argentic chloride and metallic silver.

*Argentic chloride*, or *Chloride of silver* ( $\text{AgCl} = 143.5$ ); *Sp. Gr.* 5.552; *Comp. in 100 parts*, Ag, 75.27; Cl, 24.73.—This compound is found native, either crystallized in cubes, or as a compact semi-transparent mass, known by the name of *horn silver*. It is procured as a dense white flocculent precipitate on adding hydrochloric acid or the solution of any chloride to a soluble salt

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\* Argentic nitrate forms with the sulphide a yellow compound,  $\text{Ag}_2\text{S}, \text{AgNO}_3$ , insoluble in cold nitric acid, but it is decomposed when washed with boiling water. It is left in the form of a yellow powder when silver containing sulphide is dissolved in warm nitric acid of sp. gr. about 1.2.

of silver: when moist it quickly assumes a violet colour by exposure to the sun's light; a similar change is produced gradually by diffused daylight. The subchloride appears to be formed under these circumstances, and chlorine is set free. If the chloride be moistened with a solution of argentic nitrate and exposed to the sun in a thin layer, a strong odour of hypochlorous acid is immediately developed.

Argentic chloride is insoluble in pure water, and in all the diluted acids. A solution of silver containing not more than 1 part of the metal in 200,000 of water is immediately rendered opalescent by the addition of hydrochloric acid. Argentic chloride is however taken up by boiling hydrochloric acid and by strong solutions of the chlorides of metals of the alkalies and alkaline earths, with which it forms crystallizable double salts; they are decomposed if their solutions are diluted; advantage is taken of this circumstance in the extraction of silver (p. 755). Argentic chloride is decomposed by digestion with a solution of potassic bromide or iodide, argentic bromide or iodide being produced, while potassic chloride is obtained in solution. Field, by whom this result was observed (*Q. J. Chem. Soc.* x. 236), has proposed to employ it for determining the proportions of chlorine, bromine, and iodine in the analysis of a mixture in which they occur together.

Argentic chloride melts at a temperature of about  $500^{\circ}$  ( $260^{\circ}$  C.), and when strongly heated it is partially volatilized; on cooling it forms a horny, semi-transparent, sectile mass. It is not decomposed when heated with carbon; but it is easily reduced by hydrogen if it be heated in a current of the gas, hydrochloric acid being formed, while metallic silver is set free; zinc, and iron, and many of the easily oxidizable metals, also reduce moist argentic chloride. On the large scale this process is turned to account in the refining of silver (940). It is not necessary that the argentic chloride be freshly precipitated, though, if it be, the operation is more rapid; if a cake of the fused chloride be laid upon zinc or on iron and covered with acidulated water, it will after some days be completely reduced to a spongy mass of metallic silver.

Weak alkaline leys do not act upon argentic chloride, but if a concentrated solution of potash be boiled upon it, potassic chloride is formed, and a dense black argentic oxide is produced; the addition of sugar to this mixture reduces the oxide rapidly to the state of metallic silver. A solution of ammonia dissolves the chloride freely, and deposits it again, by evaporation at ordi-

nary temperatures, in transparent colourless crystals; if the solution be boiled with potash, fulminating silver is deposited. The ammoniacal solution also readily furnishes metallic silver if it is poured very slowly into a boiling solution of 5 parts of grape-sugar, and 15 of crystallized sodic carbonate in 200 of water for every 4 parts of argentic chloride. If the liquid be kept boiling during the whole time, the silver is deposited in the form of a yellowish grey powder which is easily washed clean. The solid chloride absorbs ammoniacal gas rapidly, and leaves it unaltered when heat is applied (369). When argentic chloride is ignited with the carbonates of the alkali-metals, chlorides of these metals are formed and pure silver is left; this reaction furnishes a means of procuring large quantities of silver in a state of purity;  $4\text{AgCl} + 2\text{Na}_2\text{CO}_3 = 4\text{NaCl} + 2\text{CO}_2 + \text{O}_2 + 2\text{Ag}_2$ . Argentic chloride is soluble in solutions of the hyposulphites, forming compounds of an intensely sweet taste: by evaporating these solutions crystalline double hyposulphites may be procured (419). Potassic cyanide likewise dissolves argentic chloride, forming potassic chloride and argento-potassic cyanide ( $\text{KCy}, \text{AgCy}$ ). The soluble sulphites also dissolve argentic chloride.

(945) ARGENTIC BROMIDE, or *Bromide of silver* ( $\text{AgBr} = 188$ ); *Sp. Gr.* 6.353; *Comp. in 100 parts*, Ag, 58.53; Br, 41.47.—This constitutes a rare mineral which has been found in Chili; but it occurs mixed in tolerable abundance at the mine of Chañarcillo, in Atacama, with argentic chloride in variable proportions. The bromide may be formed artificially by adding a solution of potassic bromide to one of argentic nitrate. It is of a yellowish colour, is insoluble in water, and is much less soluble in ammonia than the chloride. Acids do not dissolve it, but chlorine disengages vapours of bromine from it, and argentic chloride is produced. Argentic bromide fuses below a red heat. It is soluble in a concentrated solution of potassic bromide, and in other bromides, with which it forms double salts, which are decomposed by dilution with water. Argentic bromide is soluble in a solution of sodic hyposulphite.

(946) ARGENTIC IODIDE, or *Iodide of silver* ( $\text{AgI} = 235$ ); *Sp. Gr.* 5.5; *Comp. in 100 parts*, Ag, 45.96; I, 54.04.—This compound is found in Mexico, mixed with calcic carbonate, native silver, and plumbic sulphide. It may be procured artificially by precipitating a solution of argentic nitrate by one of potassic iodide, when a pale yellow, flocculent deposit occurs, which is but slowly acted on by light, is insoluble in acids, and almost so in ammonia. It may also be obtained by acting upon metallic

silver with hydriodic acid, which dissolves the metal with evolution of hydrogen, and gradually deposits six-sided prisms of the iodide. It fuses easily into a mass which becomes yellow and opaque on cooling. It is decomposed by zinc in the presence of moisture. Chlorine displaces the iodine from the salt. Argentic iodide is soluble in a hot solution of hydriodic acid, which on cooling deposits flaky crystals of a compound of the acid with argentic iodide ( $\text{AgI} \cdot \text{HI}$ ). The iodide is likewise soluble in concentrated solutions of potassic iodide, as well as in those of sodic hyposulphite.

ARGENTIC FLUORIDE, or *Fluoride of silver* ( $\text{AgF} = 127$ ), is freely soluble in water; it is obtained by dissolving argentic oxide or carbonate in diluted hydrofluoric acid, but it is partially decomposed on evaporating its solution.

(947) ARGENTIC SULPHATE, or *Sulphate of silver* ( $\text{Ag}_2\text{SO}_4 = 312$ ); *Sp. Gr.* 5.322; *Comp. in 100 parts*,  $\text{Ag}_2\text{O}$ , 74.36;  $\text{SO}_3$ , 25.64.—When silver is boiled with sulphuric acid, a portion of the acid is decomposed and gives oxygen to the silver, which is converted into a sulphate, while sulphurous anhydride escapes: the sulphate is dissolved by the excess of acid, but is deposited in great part on the addition of water, of which it requires 90 times its weight for solution. It may be obtained in small rhombic prisms, which are isomorphous with those of anhydrous sodic sulphate. They fuse readily; for their decomposition they require a temperature higher than is needed to decompose the sulphates of iron or copper (p. 755.) Small quantities of gold are separated from silver on the large scale, by boiling 1 part of the alloy, finely granulated, in cast-iron vessels with  $2\frac{1}{2}$  parts of oil of vitriol; the gold is left behind as a fine powder. The solution of silver is afterwards diluted till of a specific gravity of 1.200, introduced into leaden vessels, and the silver precipitated in the metallic form from the solution by bars of metallic copper. This process has been economically applied to the extraction of the gold contained in old silver coin, even where the proportion of gold did not exceed 1 part in 2000. It cannot be advantageously practised upon alloys containing more than about 200 parts of gold per 1000. If copper be present, its proportion should not exceed 4 per cent. of the mass; otherwise the cupric sulphate, owing to its sparing solubility in the acid, impedes the operation. Crystallized argentic sulphate rapidly absorbs ammonia, to the extent of 2 atoms for each atom of the salt. A hot solution of ammonia dissolves the salt freely, and on cooling deposits crystals composed of  $(4\text{H}_3\text{N} \cdot \text{Ag}_2\text{SO}_4)$ .

A *silver alum* ( $\text{AgAl}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ ) may, according to Church, be obtained in octohedral crystals by heating argentic sulphate and aluminic sulphate in equivalent proportions with a little water, until the silver salt has become dissolved. An excess of water separates it into its component salts.

(948) ARGENTIC NITRATE, or *Nitrate of silver* ( $\text{AgNO}_3 = 170$ ); *Sp. Gr.* 4.336; *Comp. in 100 parts*,  $\text{Ag}_2\text{O}$ , 68.23;  $\text{N}_2\text{O}_5$ , 31.77, or  $\text{Ag}$ , 63.51.—This salt is readily formed by dissolving silver in moderately strong nitric acid. If standard silver be employed in its preparation, the cupric oxide is easily separated from the solution by boiling it upon freshly precipitated argentic oxide, which may be obtained by precipitating a portion of the same solution by caustic potash, and washing the precipitate, the presence of cupric oxide being unimportant. It crystallizes in square, colourless, anhydrous tables, which require an equal weight of cold water for solution. Boiling alcohol dissolves about a fourth of its weight of the salt, but deposits most of it on cooling. The nitrate fuses at  $426^{\circ} \cdot 2$  ( $219^{\circ} \text{C.}$ ) when heated, and if then cast into cylindrical moulds, it forms the sticks of *lunar caustic* (from *luna*, the alchemical name for silver) employed by surgeons as an escharotic. By a more elevated temperature it is decomposed, argentic nitrite is produced, and at a still higher temperature metallic silver is left.

Argentic nitrate, when pure, undergoes no change by the action of light; but it is readily decomposed by the combined action of light and organic matter, which last it usually stains black. The stain thus produced cannot be removed by washing with soap and water; from this property it has been employed as the basis of an ink for marking linen, which may be prepared as follows:—Dissolve 10 grammes of argentic nitrate and 5 grms. of gum arabic in 35 c. c. of water, and colour the liquid with Indian ink. It is requisite to prepare the cloth first, by moistening the spot to be marked with a solution of sodic carbonate, which is allowed to become dry. This preparatory solution may consist of 80 grms. of crystallized sodic carbonate, and 10 grms. of gum, dissolved in 160 c. c. of water.\* The black stains of argentic nitrate may be removed from the hands or from linen, by the employment of a strong solution of potassic iodide; potassic cyanide is still more effectual. Dry argentic nitrate absorbs 3 atoms of ammonia, and if ammoniacal gas be passed into a concentrated solution of the salt, crystals having the composition ( $2\text{H}_3\text{N}, \text{AgNO}_3$ ) are deposited.

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\* A solution of coal-tar in naphtha forms a cheap indelible marking ink, which resists the action of chlorine, and is used by bleachers to mark their goods.

When metallic silver in fine powder is digested in a solution of argentic nitrate, it is dissolved, and a yellow solution is formed analogous to that obtained when lead is similarly treated (905).

(949) TRIARGENTIC PHOSPHATE, or *Triphosphate of silver* ( $\text{Ag}_3\text{PO}_4 = 419$ ; *sp. gr.* 7.321), is of a yellow colour, which is speedily changed by the action of light. The salt is very soluble in excess both of nitric acid and of ammonia. It is easily procured by precipitating a solution of the ordinary hydrodisodic phosphate by one of argentic nitrate; it fuses if heated above redness. *Argentic pyrophosphate* ( $\text{Ag}_2\text{P}_2\text{O}_7$ ; *sp. gr.* 5.306) is obtained in like manner by precipitating argentic nitrate by sodic pyrophosphate; it is a white precipitate slowly darkened by light, and is easily fusible. The *metaphosphate* ( $\text{AgPO}_3$ ) is obtained by precipitation from the argentic nitrate by solutions of sodic metaphosphate; it forms a gelatinous mass, which softens even at a heat of  $100^\circ \text{C.}$ , and is soluble in excess of argentic nitrate. If boiling water be poured upon this precipitate, it fuses; acid is removed, and a submetaphosphate is left, consisting of ( $\text{Ag}_2\text{P}_2\text{O}_7$ , or  $3\text{Ag}_2\text{O}, 2\text{P}_2\text{O}_5$ ).

(950) CHARACTERS OF THE SALTS OF SILVER. — The soluble salts of this metal are colourless, and nearly all are anhydrous; they do not redden litmus; they have a powerfully acrid, metallic, astringent taste, and act as irritant poisons. *Before the blowpipe* they are all readily reduced on charcoal to the metallic state, especially when mixed with sodic carbonate. They give a yellowish bead with microcosmic salt in the oxidating flame. In solution the salts of silver present the following reactions:—

The *hydrates of the fixed alkalis* give a brown hydrated oxide, insoluble in excess of the precipitant; *ammonia*, a brown precipitate, readily soluble in excess of ammonia; *potassic* and *sodic carbonates*, a white argentic carbonate insoluble in excess, but soluble in ammoniac sesquicarbonate. *Sulphuretted hydrogen* and *ammonic hydrosulphide* give a black precipitate of argentic sulphide, not soluble in ammonia or in the sulphides of the alkali-metals. But the most characteristic test is the action of *hydrochloric acid*, or of a *soluble chloride*, which produces a white curdy precipitate of argentic chloride, insoluble in nitric acid even when boiling, but readily soluble in ammonia; it is also soluble in sodic hyposulphite, with which it forms an intensely sweet solution; potassic cyanide also dissolves it: argentic chloride speedily assumes a violet tinge when exposed to light; this change is impeded by the presence of free chlorine as well as by that of free nitric acid, and is prevented by the admixture of a small proportion of mercuric chloride. *Potassic iodide* or *bromide* gives a yellowish-white precipitate of argentic iodide or bromide, sparingly soluble in ammonia. *Hydrocyanic acid* and *potassic cyanide* give a white curdy precipitate of argentic cyanide, which is soluble in excess of



potassic cyanide, easily soluble in ammonia, insoluble in diluted nitric acid, but soluble in boiling nitric acid if concentrated. *Phosphoric, chromic, oxalic, tartaric, and citric* acids, all form insoluble precipitates with salts of silver. Indeed, silver furnishes a greater number of insoluble salts than any other metal; they are almost all neutral in composition, and generally of a dazzling white appearance. Most of them, however, become black when exposed to the action of light. Nearly all of them are soluble in ammonia, and many of them also in nitric acid. *Many metals* reduce solutions of the salts of silver, and throw down the silver from them in a metallic state, as is beautifully shown by the action of mercury, which produces a crystalline deposit consisting of an amalgam of silver, forming what has been termed the *arbor Dianæ*.\* Copper and zinc also precipitate silver from its solutions. *Phosphorus* becomes coated with metallic silver if placed in a solution of any of its salts. A solution of *ferrous sulphate* also precipitates silver in the metallic form from its solutions, if they do not contain free nitric acid. If a solution of ammonianitrate of silver be added to one of ferrous sulphate, an intensely black precipitate ( $\text{Ag}_4\text{O}_2\text{FeO}_2\text{Fe}_2\text{O}_3$ ; H. Rose) is produced. This reaction is extremely sensitive for very small quantities of iron.

The compounds of silver exhibit a less strongly marked tendency to form double salts than is the case with the other noble metals.

(951) *Estimation of Silver*.—Silver may be estimated either in the metallic state, as in the process of cupellation,—or in the form of chloride, 100 parts of which, after fusion, correspond to 75.27 of the metal. This precipitation is best effected by acidulating the liquid with nitric acid, and adding hydrochloric acid in slight excess. After the precipitate has been collected and dried, it should be detached from the filter, and fused in a porcelain capsule; on burning the filter, the portions of chloride retained by it are reduced partially to the metallic state by the hydrogen of the paper; the ash must therefore be moistened, first with nitric, and then with hydrochloric acid, to reconvert it into chloride: the excess of acid must afterwards be expelled by heat.

(952) *Separation of Silver from other Metals*.—This is readily effected by means of hydrochloric acid. If lead be present, the solution must be diluted largely: should mercury be in solution, it must be converted into a mercuric salt by boiling the liquid

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\* On one occasion I found the long prismatic thin crystals to have the composition  $\text{Ag}_4\text{Hg}_2$ , containing 26.45 per cent. of metallic silver.

with nitric acid, after which the silver may be precipitated in the form of chloride.

§ III. GOLD (Aurum):  $Au=196\cdot6$ . *Sp. Gr.*  $19\cdot34$ ; *Fusing-point*,  $2016^{\circ}$  ( $1102^{\circ}\cdot2$  C.); *Monad in Aurous salts*, as  $AuCl$ ; *Triad in Auric salts*, as  $AuCl_3$ .

(953) THIS valuable metal has been prized from the earliest ages of the world. It is found in small quantities in numerous localities, and always occurs in the native state, either crystallized in cubes, octohedra, or tetrahedra,—or in plates, in ramified masses, or in nodules or *nuggets*, which sometimes weigh many kilogrammes.\* Native gold is always alloyed with silver; sometimes small quantities of osmium and iridium, copper, antimony, and, in some rare instances, tellurium, are found accompanying it. No regular veins of gold are met with; it commonly occurs either in primitive or volcanic rocks, or in the alluvial deposits of certain rivers. Its most celebrated mines are those of California and Australia; and those of Mexico, Chili, Brazil, and Peru. In California the gold is chiefly found upon the Sacramento and its tributary streams, in deposits formed by the disintegration of quartz and granite. In Australia the gold is also associated with quartz, and occurs in slate rocks equivalent to the Cambrian formations of England and Wales, in the detritus of which the most productive gold-fields occur, in the deep gullies at the base of the rocky ranges of clay-slate, mica schist, red and yellow sandstone. In this alluvium the gold is usually found at a depth of from 10 to 40 feet (3 to 12 metres), resting upon a 'bottom' of pipeclay. A good deal of gold is still obtained from the Ural Mountains; gold mines have also been worked in Wales, in the Cader Idris district. Many of the rivers of Africa likewise contain it among their sands, as do those of Hungary, Transylvania, and Piedmont: in these European countries it is principally extracted from the river sands by gipsies.

*Extraction.*—The operations for obtaining gold from its deposits differ from those required by almost every other metal, in being for the most part purely mechanical. According to Mr. Wathen (*The Golden Colony*, p. 71), the Australian digger formerly used a *cradle* for washing the ore, but this is not adapted to the stiff clays of the Australian gold-fields. The miner now, after

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\* A specimen of native gold, nearly free from earthy impurities, from the Kingower diggings, Australia, weighing 1743 oz., was exhibited in England in the early part of 1858, and still larger masses have been found subsequently.

having raised the 'washing stuff' from the pit, introduces it into the 'puddling tub,' which is merely one-half of a porter-cask. The tub is half filled with the washing stuff, water is baled in from the creek, and the whole worked about with the spade until the clay has become diffused through the water; this turbid water is poured off, and fresh water added, until, by repetition of the washing, "nothing but clean gravel, sand, and gold remains. The gold is now readily separated from the gravel by means of a cradle, or simply by a tin dish. In the latter case, the dish is held half-immersed obliquely in water, and the gravel gradually washed away from the gold by the dexterous handling of the dish."

The Californian 'Long Tom' consists of a trough about 16 inches (0·4 metre) wide, and 10 or 12 feet (3 or 4 metres) long, inclined so as to cause the water to run rapidly down: an iron grating, perforated with holes as large as a sixpence, forms the lower end, and is tilted in an opposite direction to the trough. Through the trough a current of water is kept constantly flowing. The auriferous earth is thrown in at the head, and as it is washed down by the stream, it is worked about with the spade; the earth and clay are quickly washed away; when the clean gravel reaches the lower end, it is arrested by the iron grating, and removed with a shovel, while the gold and sand fall through into a box placed beneath. The contents of the box are again washed to extract the gold.

Auriferous quartz is first crushed, then stamped and ground to powder, and from the powder the gold is subsequently extracted by amalgamation.

Much of the gold in circulation before the discovery of the deposits in Australia and California was obtained from auriferous pyrites. This mineral is coarsely pulverized, either before or after roasting, and washed: the heavier particles of gold subside, and are extracted from this concentrated portion by amalgamation, the excess of mercury being separated by distillation.\* Various methods are adopted for washing the auriferous material: in Mexico this operation is usually performed by negroes, who having pulverized the ore under flat stones, agitate it in wide, shallow, wooden dishes, separating the lighter portions with much dexterity. In Europe, the pyrites is ground and amalgamated, in mills constructed for the purpose. Those who wash the river sands usually select some spot at the bend of the stream, where the mud appears to be black or reddish; as it is here, if anywhere, that the gold is found. The most favourable time is when the waters are subsiding after storms or heavy rains: the sand is

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\* Mr. Crookes has shown that the amalgamation is greatly facilitated by adding to the mercury a small proportion of an alloy of sodium and zinc. The sodium enables the mercury to wet the surface of the gold immediately, and diminishes the loss of both gold and mercury in the process.

concentrated either by washing it in shallow vessels, or else by allowing it to pass through a succession of troughs. Amalgamation is afterwards resorted to, and the product is distilled, as in the analogous process for obtaining silver.

(954) *Properties*.—Gold is of a rich yellow colour and high metallic lustre. It is not remarkable for its hardness, being, when in a pure state, nearly as soft as lead. Its ductility, however, is considerable, ranking next to silver, so that it may be drawn into very fine wire.

As already mentioned, it is the most malleable of the metals, and so extreme is the thinness to which it may be reduced by hammering, that 280,000 leaves placed upon one another would be required to occupy the thickness of one inch (or 11,200 in a millimetre). The thickness of the film may be still further reduced by floating it upon a dilute solution of potassic cyanide. Faraday found that such a film when attached to a plate of glass still retained its power of reflecting yellow light and transmitting green: if, however, the temperature were maintained for a short time at a point which need not exceed  $600^{\circ}$  ( $316^{\circ}\text{C.}$ ), the metallic lustre disappeared entirely, and the transmitted light became of a pure ruby red. The pressure of agate, or of any kind of hard body upon the film, changed the colour of the transmitted light at that spot again to green. (*Phil. Trans.* 1857, 147.)

Gold fuses at a temperature of  $2016^{\circ}$  ( $1102^{\circ}\text{C.}$ ) It cannot be advantageously employed for castings, as it shrinks greatly at the moment of solidifying. It is but very slightly volatile in the heat of the furnace, though by a powerful electric discharge, by the concentration of the sun's rays with a large convex lens, or by the intense heat of the oxyhydrogen jet, it may be dispersed in purple vapours. It is one of the most perfect conductors both of heat and of electricity. Gold suffers no change by exposure to air and moisture at any temperature. None of the simple acids, with the exception of the selenic, has any effect upon it, but it is dissolved by any mixture which liberates chlorine. Its usual solvent is aqua regia, which for this purpose is generally prepared by mixing 1 part of nitric acid and 4 parts of hydrochloric acid. The hydrated alkalies do not affect it; a crucible of gold is consequently a valuable instrument in the analysis of minerals which require fusion with the caustic alkalies. The metal combines directly with fluorine, chlorine, and bromine, without the aid of heat, and with phosphorus when heated.

(955) *Preparation of Fine Gold*.—Gold is best obtained in a state of purity by dissolving the metal in aqua regia, and evaporating the solution of auric chloride thus obtained with an excess of hydrochloric acid, for the purpose of destroying the excess of nitric acid: the solution is then largely diluted with water, to precipitate the argentic chloride, from which it is afterwards decanted. A solution of ferrous sulphate is next prepared and

added to the solution of auric chloride: 1 part of gold requires between 4 and 5 parts of the crystallized sulphate [ $6\text{FeSO}_4 + 2\text{AuCl}_3 = 2(\text{Fe}_2\text{SO}_4) + \text{Fe}_2\text{Cl}_6 + 2\text{Au}$ ]. Metallic gold is thus precipitated in the form of a finely divided powder, which, when suspended in water, is brown by reflected, but purple when viewed by transmitted light. For commercial purposes it would be sufficient now to collect the gold, dry it, and after fusing it with borax, to cast it into ingots; but when required to be perfectly free from silver, the gold is not melted at this stage, but the precipitated metal is boiled with hydrochloric acid of sp. gr. 1.1. The acid is decanted, and the residue is boiled twice with fresh acid without washing the gold between these successive additions of acid. The last traces of iron and nearly all the argentic chloride are thus removed. The gold is then washed, dried, and mixed with its own weight of hydropotassic sulphate, and fused in a Hessian crucible. The last portions of argentic chloride are thus removed, and the gold is perfectly pure. When thus prepared its surface often exhibits a crystalline appearance, being embossed with aggregations of tetrahedra if the metal be allowed to cool slowly.

Levol prefers to precipitate the gold from an acid solution of its chloride by means of an acid solution of antimonious chloride:  $3\text{SbCl}_3 + 2\text{AuCl}_3 = 3\text{SbCl}_5 + 2\text{Au}$ . The hydrochloric solution retains any traces of argentic chloride which may be present.

*Uses.*—Gold is employed in its finely divided state for gilding porcelain, which is first painted with an adhesive varnish and allowed to become partially dry; the powdered metal is then, dabbed on with a dry pencil (having been previously mixed with a fusible enamel), after which the article is fired; the gilt portions are subsequently burnished, and take a high polish. It communicates a fine ruby colour to glass, and is the colouring ingredient in the beautiful red glass manufactured in Bohemia. The uses of gold in the fabrication of ornamental articles and in coinage are well known; like silver, it is too soft to be employed in a pure state.

(956) *Gilding* upon woodwork, papier-mâché, or plaster, is effected by means of gold-leaf, which is attached to the surface by an adhesive varnish, such as gold-size. Gilding upon metals is effected either through the medium of mercury, as in one of the processes for silvering (935), or by voltaic action, as in the operation of electro-silvering already mentioned: for this purpose, a solution either of the auro-potassic cyanide ( $\text{AuCyKCy}$ ), or of auro-potassic sulphide ( $\text{AuKS}$ ), is used (296).

With mercury, gold forms a semi-solid amalgam of a yellowish colour, which is soluble in an excess of mercury. This excess may be removed, as in the case of silver amalgam, by filtering, and squeezing it through chamois leather. It is this amalgam which is formed during the extraction of gold from its ores; it is also extensively prepared for the purposes of gilding. A combination of mercury with gold ( $\text{Au}_8\text{Hg}$ ) may be obtained crystallized in brilliant four-sided prisms by acting with diluted nitric acid, aided by a gentle heat, upon an amalgam of gold containing about 1 part of gold to 1000 of mercury (T. H. Henry): these crystals are insoluble in nitric acid.

(957) *Alloys of Gold*.—The ductility of gold is much impaired by alloying it with other metals, though its hardness and sonorousness are increased: these alloys are generally formed without difficulty. If a proportion of tin, of cobalt, of nickel, or of zinc, greater than 2 per cent. of the mass be present in the alloy, it is unfit for coinage; and still smaller quantities of lead, of arsenicum, of antimony, or of bismuth, render gold brittle. Palladium is a still more inconvenient impurity, since it not only renders the gold brittle, but it requires special treatment in order to extract it, as it is not removed by the ordinary operations of the refiner. A similar remark is applicable to the alloy of platinum with gold. Small quantities both of platinum and of palladium render the gold nearly white. The native alloy of osmium and iridium, which frequently accompanies the Californian gold, does not combine with the metal, but remains disseminated through it in distinct grains after the gold has been melted. These grains occasion much inconvenience; they often escape notice until the metal passes through the coining press, where they make themselves apparent by their hardness, and by the injury which they consequently inflict upon the dies.

Silver and gold may be alloyed with each other in all proportions. The alloy which they form has a pale greenish-yellow colour, but it becomes nearly white when the quantity of silver exceeds 50 per cent. The malleability of gold is less diminished by the presence of silver than by that of any other metal. In the arts it frequently becomes necessary to separate these two metals, and this is usually effected by the method termed *quartation* or *parting*. This operation depends on the solubility of silver in nitric acid, and the insolubility of gold in this liquid. It is necessary that the silver should amount to at least three times the weight of gold, otherwise portions of silver would be protected mechanically from the action of the acid, and the sepa-

ration would be incomplete. If, therefore, the alloy be found to contain more than a fourth of its weight of gold, sufficient silver is added to reduce it to this proportion, and hence the origin of the term 'quartation.' The metals are fused together, granulated by being poured into water, and they are then digested in the acid. The gold is afterwards melted into ingots, the silver is precipitated as chloride, by common salt, and the chloride is reduced either by zinc (940), or by fusion with an alkali (944). On the large scale sulphuric acid is usually substituted for nitric acid; it is much cheaper, and is quite as effectual in dissolving the silver if boiled upon it (947). Indeed, in refining upon the large scale, when sulphuric acid is used the gold may be obtained containing 998 or 999 thousandths of the pure metal; whereas when nitric acid is used it is seldom finer than from 993 to 995 thousandths.

Silver and many other metals may also be removed from gold by forcing through the melted metal a current of chlorine gas: argentic chloride forms, and collects upon the surface, whilst the chlorides of arsenic, antimony, bismuth, and zinc are volatilized if these metals are present (F. B. Miller).

The most useful alloy of gold is that which it forms with copper; it is of a redder colour than pure gold, and considerably harder and more fusible, but it is less ductile and malleable. It is this alloy which is used for coinage. British standard gold contains 8.33 per cent. of copper, or 11 parts of gold to 1 part of copper. The specific gravity of this mixture is 17.157, instead of 18.47, the two metals expanding a little when they unite. In France and in the United States the standard gold contains 10 per cent. of copper. Jewellers frequently alloy their gold with a mixture of copper and silver. The alloys of gold and copper, when once the materials have been well mixed, do not exhibit the tendency to liquation which occasions so much trouble in the case of silver (937). The solder used for uniting pieces of gold is an alloy of gold with copper, which melts at a lower temperature than pure gold.

(958) *Assay of Gold*.—In the assay of gold, a combination of the processes of cupellation and quartation is employed. In the cupellation of gold the quantity of lead which is needed is about double that employed for silver: 1 part of copper requiring about 32 parts of lead. The assay of gold furnishes results which are more accurate than those obtained in the cupellation of silver. The loss of gold by volatilization is very much smaller, and scarcely any of the metal is carried into the cupel by an excess of lead.

The following is an outline of the method adopted in the assay of gold:—The quantity of the alloy for assay (usually

0.5 grm.) having been accurately weighed, it is wrapped in a piece of paper, with a proportion of silver equal to about 3 times that of the gold which the alloy is supposed to contain,\* and this is submitted to cupellation in the manner already described when speaking of the assay of silver (938). By this means the silver and the gold become thoroughly incorporated, and the copper is oxidized and absorbed by the cupel with the oxide of lead. The auriferous button is then hammered into a flattened disk, of about the size of a sixpence, and annealed, by heating it to redness. It is next passed between a pair of laminating rollers, by which its thickness is reduced to that of an ordinary address card, after which it is a second time annealed. These operations render it sufficiently flexible to allow of its being coiled into a small spiral by rolling between the finger and thumb. The *cornet* thus obtained is next introduced into a flask which contains about 30 grammes of nitric acid of sp. gr. 1.180, heated nearly to the boiling-point. Brisk evolution of nitrous fumes immediately ensues; the silver is gradually dissolved away, and the gold is left in the form of the original cornet, as a brown, porous, very brittle mass. After this first boiling has been continued for 10 minutes, the flask is removed from the fire, the acid solution is poured off, and the cornet is washed by carefully pouring distilled water upon it; and this water, after standing for a couple of minutes, is again poured off. Some traces of silver are, however, still retained by the gold, and, in order to remove these, the cornet is again boiled with nitric acid, which, this time, must be of sp. gr. 1.280. In this second boiling, which must be continued for 20 minutes, a small fragment of charcoal or a pellet of baked fireclay should be introduced into the flask, in order to prevent the ebullition from taking place irregularly, with sudden bursts, as it is very apt to do if this precaution be neglected.

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\* An approximative estimate of the composition of the alloy is sometimes made by the use of the touchstone, though it is seldom employed by the practised assayer:—A number of pieces of alloy are formed containing known quantities of gold and copper, or of gold and silver: the first consisting of pure gold; the second of 23 parts of gold and 1 part of copper; the third of 22 of gold and 2 of copper, and so on: the assayer selects one of these alloys, or 'needles,' which from its colour he judges to approach nearest in composition to the alloy which he is about to assay; this he rubs upon a hard, black stone, the 'touchstone,' which is a peculiar kind of bituminous quartz formerly obtained from Lydia, in Asia Minor; black basalt, however, may be employed for the purpose: the alloy leaves a streak upon the stone, the colour of which is redder in proportion as the copper preponderates. The streak formed by the alloy for assay is then compared with that of the needles, until one of these is found to which it nearly corresponds. The judgment may be further aided by moistening the streaks obtained with a little nitric acid, which attacks the copper or silver, but leaves the gold.



The acid having been poured off, the flask is filled up completely with distilled water. A small, smoothly finished, porous clay crucible is placed over the mouth of the flask, and the flask and crucible are inverted, so that the cornet shall fall gently through the water into the crucible: by a dexterous movement of the hand, the flask is then withdrawn in such a manner as to prevent the overflow of any liquid from the little crucible; the water is afterwards carefully poured off from the cornet, and the crucible is heated to redness in the muffle. By this means the gold, though it is not fused, is rendered much more compact; it shrinks in bulk, loses its brown appearance, and assumes the peculiar colour and lustre of the metal. When cold, the cornet is weighed with the same precision as the original alloy. The assayer calls the arbitrary weight of the alloy upon which he operates, 1000; his weights are all subdivided so as to give him the value of the alloy in thousandths of this original quantity: so that if he find a portion of the alloy which originally weighed 1000 of these arbitrary units, to yield a quantity of gold equal to  $916\frac{2}{3}$  of these parts, he reports it as 916.6. 1000 ounces of such an alloy would contain 916.6 ounces of fine gold.

The amount of alloy upon which it is most convenient to operate in assaying is half a gramme, or between 7 and 8 grains.

The gold contained in the cornet is never absolutely pure: it retains a small quantity of lead and of silver, and frequently also traces of copper, which render its weight a little higher than it ought to be. In order to ascertain the amount of this error, a number of *proofs* are passed through the muffle simultaneously with the alloys, and subjected to the same process as the alloys themselves. These proofs consist of weighed portions of fine gold, to each of which is added a proportion of copper equal to that estimated to exist in the alloys under examination. The excess of weight which these proofs indicate shows the amount of the correction which it becomes necessary to make. This correction is liable to daily variation, according to the temperature of the furnace, the more or less perfect softening of the buttons during annealing, the thickness of the cornets, &c.; but it usually varies from 0.2 to 0.5 parts in 1000. Most assayers vary the quantity of lead according to the proportion of copper in the alloys. I have found it advantageous to use the same amount of lead in all cases; the correction then becomes uniform for all the assays passed at one operation.

When the alloy contains very little copper, as commonly occurs with native gold, the button of alloy is liable 'to spit' as it cools after the cupellation; this mischance may easily be prevented by the addition of a small fragment of copper, not exceeding 50 mgrms. in weight, before introducing the alloy into the cupel.

It frequently happens that it is necessary to ascertain the proportion both of gold and of silver in a given alloy. If the proportion of gold preponderate, the quantity of gold is determined in the manner above described, and that of the gold and silver together is ascertained by submitting a portion of the alloy to cupellation with lead, as if it consisted of silver only (938). The two metals, gold and silver, remain upon the cupel, whilst the copper and more oxidizable metals are absorbed. The weight of the residual button gives the united weight

of the gold and silver, and the difference between this weight and that of the gold alone will of course furnish the proportion of silver.

When the proportion of gold is very small compared with that of the silver, the two metals are treated with nitric acid at once, without submitting them to the usual assay for gold; the acid dissolves the silver and other metals which may be present, leaving the gold in the form of a black powder: this powder must be collected by subsidence in one of the small porous crucibles used for annealing gold cornets, in which it is ignited, and can afterwards be weighed without difficulty.

(959) OXIDES OF GOLD.—There are two oxides of gold: a suboxide,  $\text{Au}_2\text{O}$ , and a sesquioxide,  $\text{Au}_2\text{O}_3$ : the latter when hydrated possesses acid properties, and is frequently termed auric acid.

*Aurous oxide*, or *Suboxide of gold* ( $\text{Au}_2\text{O}=409\cdot2$ ), is obtained as a dark green powder by precipitating aurous chloride with a dilute solution of potash; it is slightly soluble in excess of the alkali: when digested with ammonia it forms fulminating gold: hydrochloric acid converts it into metallic gold and auric chloride. Aurous oxide undergoes a suspension in pure water, and passes through the filter; but boiling the solution after adding any saline compound causes its precipitation.

*Auric oxide*, *Peroxide of gold* ( $\text{Au}_2\text{O}_3=441\cdot2$ ).—This compound is best obtained by decomposing a solution of auric chloride by magnesia; for if solutions of the alkalies be used, they adhere strongly to the precipitate: it falls in combination with the earth, which may be removed by means of diluted nitric acid, and auric oxide remains as a yellow hydrate, if the acid used be weak, or as a brown anhydrous powder if strong; it is very readily reduced by exposure to light, and at a temperature of about  $473^\circ$  ( $245^\circ \text{C.}$ ) it is resolved into metallic gold and free oxygen. It is taken up by strong nitric and sulphuric acids, but no true salts are formed; the sesquioxide being deposited again from these solutions in a pure state on dilution. Auric oxide is dissolved by hydrochloric, hydrobromic, and hydriodic acids, forming auric trichloride, tribromide, or triiodide.

Hydrated auric oxide is readily acted on by the hydrated alkalies, forming salts that have been termed *aurates*, which are soluble in water, and form yellow solutions. *Potassic aurate* crystallizes in yellowish needles ( $\text{KAuO}_2\cdot 3\text{H}_2\text{O}$ ): its solutions may be used in electro-gilding. Most of the compounds of auric acid with the earths and other metallic oxides are insoluble.

Auric oxide forms with ammonia a dark olive-brown fulminating compound, analogous to that furnished by silver (942); the same compound may be formed by adding ammonia to the trichloride, but in this case it is of a reddish-yellow colour, owing

to the admixture of a little ammoniacal subchloride of gold. So great is the attraction of auric oxide for ammonia, that it decomposes the neutral salts of ammonium, such as the sulphate, and sets the acid at liberty.

(960) *Sulphide of gold* ( $\text{Au}_4\text{S}_4=914.4$ ).—When a current of sulphuretted hydrogen is transmitted through a cold solution of auric chloride, a black precipitate is produced, which, according to Levöl, is a disulphide, or rather ( $\text{Au}_2\text{S}, \text{Au}_2\text{S}_3$ ). It is soluble in the solutions of the sulphides of the alkali-metals: its solution in disodic sulphide yields a colourless salt which is soluble in alcohol; it crystallizes in six-sided prisms, consisting of ( $\text{NaAuS}, 4\text{H}_2\text{O}$ ; Yorke),  $\text{Au}_4\text{S}_4 + 4\text{Na}_2\text{S}$  becoming  $4\text{AuNaS} + 2\text{Na}_2\text{S}_3$ . If finely divided gold be heated with sulphur in contact with potassic carbonate, a double sulphide of gold and potassium is formed; it resists a red heat, and is very soluble in water: this sulphur salt is used for gilding china, and produces the colour known as *Burgos lustre*.

(961) **CHLORIDES OF GOLD.**—Gold forms two compounds with chlorine—a protochloride,  $\text{AuCl}$ , and a trichloride,  $\text{AuCl}_3$ .

*Aurous chloride*, or *Protochloride of gold* ( $\text{AuCl}=232.1$ ).—When auric chloride is exposed to a gentle heat, it fuses, without undergoing decomposition; but if the temperature be raised to about  $347^\circ$  ( $175^\circ \text{C.}$ ), chlorine is gradually expelled, and a pale yellow, sparingly soluble powder is left, which is the protochloride. It is an unstable compound, but it may be washed with cold water to remove any undecomposed trichloride; boiling water converts it into a mixture of the trichloride with metallic gold, and a similar change is produced by exposing it to light. If the temperature be raised a little beyond  $392^\circ$  ( $200^\circ \text{C.}$ ), the whole of the chlorine is expelled. Aurous chloride, when digested in a solution of caustic potash, yields hydrated aurous oxide and potassic chloride.

*Auric chloride*, or *Trichloride of gold* ( $\text{AuCl}_3=303.1$ ); *Comp. in 100 parts*, Au, 64.86; Cl, 35.14.—This compound is produced when the metal is dissolved in aqua regia; on evaporating the solution to dryness at a temperature not exceeding  $248^\circ$  ( $120^\circ \text{C.}$ ), taking care to maintain the hydrochloric acid in excess over the nitric, this salt remains behind as a red deliquescent mass; but usually a portion of the trichloride is reduced to the state of insoluble protochloride, for it is difficult to get rid of the last portion of acid without decomposing part of the salt. It forms with water an orange-coloured solution, which preserves its colour even when very largely diluted; alcohol also dissolves the trichlo-

ride, and ether takes it up so freely as to separate it from its aqueous solution when agitated with it. Auric chloride forms a crystalline compound with hydrochloric acid; it also unites with the chlorides of many of the basylous metals to form double salts; that with potassium crystallizes in efflorescent striated prisms, consisting of  $2(\text{KCl}, \text{AuCl}_3) \cdot 5\text{H}_2\text{O}$ ; that with sodium forms four-sided prisms  $(\text{NaCl}, \text{AuCl}_3, 2\text{H}_2\text{O})$ . The chlorides of most of the organic bases also form crystallizable double salts with auric chloride: these compounds are often employed to determine the combining number of the organic alkali. Auric chloride is easily reduced by many substances; the reaction of ferrous sulphate in presence of an excess of acid has already been mentioned, so likewise has that with antimonious chloride (955). Oxalic acid produces a similar precipitate of metallic gold even in acid solutions; for instance,  $2\text{AuCl}_3 + 3\text{H}_2\text{C}_2\text{O}_4 = 2\text{Au} + 6\text{HCl} + 6\text{CO}_2$ : the powder, when viewed by reflected light, appears to be of a brown colour, but by transmitted light, whilst suspended in water, it has a purple tint. Many organic substances, if moistened with a solution of the trichloride, also exert a reducing effect upon it; hence the fingers, or writing-paper, if washed over with the solution, become stained of a violet colour when exposed to the sun's light. Metallic gold is also readily obtained from the solution of this salt by other means. A solution of sulphurous acid, or a current of the gas transmitted through the solution, or a solution of one of the sulphites, precipitates the gold completely;  $2\text{AuCl}_3 + 3\text{H}_2\text{O} + 3\text{H}_2\text{SO}_3 = 6\text{HCl} + 3\text{H}_2\text{SO}_4 + 2\text{Au}$ . Phosphorous and hypophosphorous acids, and solutions of their salts, produce the same effect; and a similar result is obtained by contact with many of the metals, such as mercury, copper, iron, and zinc. A stick of phosphorus when immersed in a solution of auric chloride soon becomes coated with the reduced metal; and if a few drops of a solution of phosphorus in ether, or in carbonic disulphide, be mixed with a very dilute solution of neutral auric chloride, containing from 30 to 60 mgrms. of the metal in a litre of water, the gold will be reduced in the course of a few hours. Provided that the bottle containing the solutions be chemically clean, the metal will be separated in particles of such extreme tenuity that it will remain suspended in the liquor for months; giving to it a ruby red or amethystine colour when viewed by transmitted light, though it appears to be turbid and brown when seen by reflected light. If this red liquid be mixed with a small quantity of a solution of common salt, the ruby tint is immediately changed to purple, the state of aggregation of the metal undergoing an instan-

taneous alteration, in consequence of which the liquid becomes colourless in a few hours, and the whole of the suspended particles of gold are deposited in a purple but perfectly metallic powder (Faraday).

(962) An *auric bromide* ( $\text{AuBr}_3$ ) crystallizes easily, and forms numerous double salts with other soluble bromides.

There are two *iodides* of gold, corresponding to the chlorides. Aurous iodide ( $\text{AuI}$ ) is a yellow insoluble powder. The auric iodide ( $\text{AuI}_3$ ) is unstable; it is green and sparingly soluble; it forms double salts with the iodides of the alkali-metals.

(963) *Purple of Cassius*.—When a mixture of stannous and stannic chloride very much diluted is added drop by drop to a dilute neutral solution of auric chloride, a flocculent purple deposit takes place. The same compound is readily formed by digesting metallic tin in a neutral solution of auric chloride; metallic gold and the purple of Cassius being formed. The true nature of this compound has been the subject of much discussion. Berzelius concluded from the researches of Figuier (*Ann. de Chimie*, III. xi. 354) that it consists of a hydrated double stannate of gold and tin ( $\text{Sn''Au}_2\text{Sn}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ ). Purple of Cassius undergoes a suspension in pure water, and passes through the filter, but it is separated on adding a salt to the liquid and boiling it. It is insoluble in solutions of potash and soda; but soluble in ammonia, forming a deep purple liquid, from which it is deposited unchanged if the ammonia be expelled by heat, or neutralized by an acid. This solution is bleached by the action of light, and gold is deposited. Purple of Cassius is decomposed by the acids, metallic gold being left; but it is not changed by the action of light. If heated to redness water is expelled, and a red powder is left, which is a mixture of metallic gold and stannic oxide. Purple of Cassius, when mixed with a little borax or some fusible glass, and applied to the surface of china, imparts to it a beautiful rose or a rich purple colour. It is this compound which is added as the colouring material in the red glass of Bohemia.

(964) *CHARACTERS OF THE SALTS OF GOLD*.—The salts of gold are recognized by the brown precipitate of metallic gold produced by *ferrous sulphate* in their acidulated solutions in the absence of free nitric acid; and by the formation of the purple of Cassius on adding to the neutral solution a dilute mixture of *stannous* and *stannic chloride*. *Metallic tin* yields the same precipitate, and is a still more delicate test. Salts of gold are reduced to the metallic state by boiling their acidulated solutions with a soluble *oxalate*, *formiate*, or *sulphite*. *Mercurous nitrate* also gives a dark brown precipitate of reduced gold. All the salts of gold are decomposed when ignited in the open air.

(965) *Estimation of Gold*.—Gold is always estimated in the metallic state. It may readily be separated from all the preceding metals by precipitating its solution by means of a solution of ferrous sulphate, after acidulating it with hydrochloric acid. The precipitate is collected upon a filter, ignited, and weighed as pure gold.

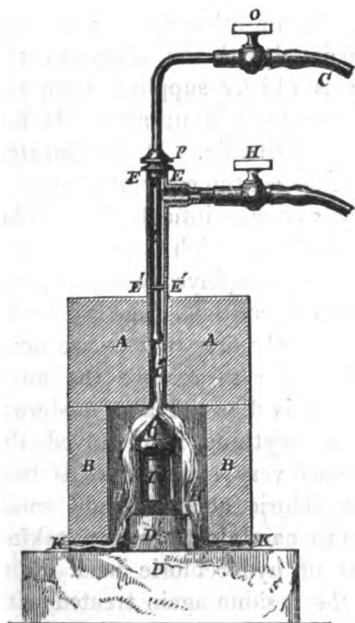
§ IV. PLATINUM: (Pt=197.1.) *Sp. Gr.* 21.5; *Dyad in Platinous salts, as*  $\text{PtCl}_2$ ; *Tetrad in Platinic salts, as*  $\text{PtCl}_4$ .

(966) PLATINUM (from the Spanish *Platina*, 'little silver') is a metal which is found in but comparatively few places: it was not recognized as a separate metal until Wood, an assayer of Jamaica, in 1741, pointed out its distinctive characters. It always occurs in the native state, usually in small flattened grains, in which it is mixed with palladium, rhodium, osmium, ruthenium, and iridium,—metals which are rarely found except when associated with platinum. Occasionally it occurs in larger nodules, frequently alloyed with gold, and traces of silver, and with copper, iron, and lead. The deposits of platinum are for the most part met with in alluvial districts associated with the débris of the earliest volcanic rocks. Platinum is chiefly supplied from the mines of Mexico, of Brazil, and of the Ural Mountains. It has also been met with in California and Australia. It is separated by washing, from the lighter impurities contained in its ore.

*Extraction*.—On account of the extreme infusibility of platinum, it requires a mode of manipulation which is complicated and peculiar. 1. The method ordinarily employed was contrived by Wollaston:—The ore, which usually contains from 75 to 85 per cent. of platinum, is treated separately first with nitric acid, and then with hydrochloric acid, in order to remove the more easily oxidizable metals, after which it is digested at a moderate heat in diluted aqua regia as long as anything is dissolved, the solution of the platinum taking place very slowly. It is best therefore to place the ore in hydrochloric acid, and add small quantities of nitric acid at intervals to maintain the action, taking care to maintain a sufficient excess of hydrochloric acid. The clear liquid is then decanted, and the residue again treated with fresh acid as long as anything is dissolved: into the mixed acid solutions a solution of sal ammoniac in 5 times its weight of water is poured (41 parts of the salt to 100 of ore): the greater part of the platinum is thus precipitated in the form of a yellow double salt ( $2\text{H}_4\text{NCl}, \text{PtCl}_4$ ), which is sparingly soluble. The mother-liquor still retains a portion of platinum, which is precipitated by

means of metallic iron; the black powder is redissolved in aqua regia, and again precipitated by the addition of sal ammoniac, the double salt thus obtained being added to the first crop. The ammonio-platinic chloride is then washed, and heated to redness, by which means the ammonia and chlorine are expelled, leaving the platinum behind in porous slightly coherent masses; this *spongy platinum* is powdered in a wooden mortar and rubbed into a magma with water, in which state it is thoroughly washed; the metallic particles soon subside, and the lighter impurities are carried away.\* This metallic mud is next poured into a somewhat conical brass mould, closed below with blotting-paper loosely supported by a plug; the greater part of the water drains off, after which the whole is subjected to the action of a very powerful press. The mass, previously of a dull grey colour, now assumes a compact metallic appearance, and acquires a specific gravity of about 10; it is next exposed to an intense heat in a wind furnace, and the ingot is forged by hammering it upon its two ends,—never upon its sides, as if this were done it would split. This heating and forging is several times repeated until the mass becomes homogeneous and ductile; it then has a specific gravity of about 21.5. Wollaston's process for working platinum depends upon its property of welding at very high temperatures. Deville and Debray, in their important memoir on platinum and the metals which accompany it (*Ann. de Chimie*, III. lvi. 385), recommend fusion of platinum by means of the oxyhydrogen blowpipe, in a cavity formed in a mass of lime, for the purpose of freeing commercial platinum from the silicon and osmium which it always contains.

FIG. 375.



The apparatus consists of the blowpipe, c, fig. 375, a furnace, A B D, and a crucible, G H I. The blowpipe is composed of a copper tube 12<sup>mm.</sup> in diameter,

\* Platinum thus prepared usually retains a small quantity of iridium, which accompanies the ammonio-platinic chloride. The platinum may be freed from this impurity by the method described in paragraph (991).

terminating below in a slightly conical platinum jet  $40^{\text{mm}}$ . (about an inch and a half) long. Within this tube, which is supplied with hydrogen through the stopcock, H, is a second copper tube, C', terminated also by a platinum nozzle with an aperture of from 2 to  $3^{\text{mm}}$ . in diameter.

The furnace, A B D, consists of three pieces of well-burnt lime of slightly hydraulic quality, which can be turned at a lathe with ease. The cylinder, A, is about  $60^{\text{mm}}$ . thick, and is perforated with a slightly conical tube, into which the blowpipe fits accurately, and is allowed to pass about half-way through the thickness of the mass. A second somewhat deeper cylinder of lime, B, is hollowed into a chamber sufficiently wide to admit the crucible and leave an interval of not more than 3 or  $4^{\text{mm}}$ . clear around it. At x x are four apertures for the escape of the products of combustion.

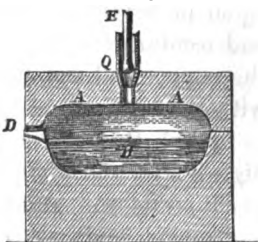
The outer crucible, H H, is also made of lime, but it contains a smaller crucible, I, of gas coke, provided with a cover of the same material, and in this the substance to be fused is placed, the crucible resting on the lime-support, D'. The conical cover, G, is made of lime, and its apex should be placed exactly under the blow-pipe jet, at a distance from it of from 20 to  $30^{\text{mm}}$ . or about an inch.

The different pieces of the furnace must be bound round with thin iron wire to support them when they crack. The oxygen is admitted under a pressure of a column of  $40^{\text{cm}}$ . (16 inches) of water. The temperature is gradually raised to the maximum, and in about 8 minutes from this time the experiment is complete.

By employing a jet of mixed coal-gas and oxygen (x q, fig. 376) in a furnace of lime, A B, provided with lip at D for pouring, Deville and Debray succeeded at an expense of from 1400 litres of oxygen or about 43 cubic feet, in melting and refining in 42 minutes, 11.595 kil. ( $25\frac{1}{2}$  lb. avoirdupois) of platinum, and casting it into an ingot in a mould of gas-coke; and much larger masses have since been melted by this method. Lime is so bad a conductor of heat, that, if a cup of lime not more than  $20^{\text{mm}}$ . thick be filled with melted platinum, the exterior scarcely rises beyond  $302^{\circ}$  ( $150^{\circ}$  C.).

2.—Deville and Debray have introduced an entirely new method for the extraction of platinum from its ores, of which the following is an outline :—A small reverberatory furnace, the bed of which is composed of a hemispherical cavity of fire-brick, lined with clay, is heated to full redness, and a charge consisting of 100 kilos., or 2 cwt. of the platinum ore, mixed with an equal weight of galena, is added in small quantities, stirring with iron rods until the platinum and lead ore have combined into a matt. A small quantity of glass is thrown in to act as flux, and by degrees a quantity of litharge equal in weight to the galena employed is added. The sulphur is thus completely oxidized and expelled, whilst the lead of the galena and the litharge is reduced to the metallic state, when it forms an easily fusible alloy with the platinum. The melted mass is now left completely at rest for some time. The osmide of iridium (which is not attacked at all during the operation) gradually sinks to the bottom of the liquid alloy, and the upper portions of the platiniiferous lead are

FIG. 376.





cautiously decanted from it by iron ladles, and cast into ingot moulds. The residue, containing the osmide of iridium, is added to a subsequent melting.

The platiniferous lead is then submitted to cupellation in the ordinary manner, and the crude metallic platinum left after cupellation is refined by fusion on a bed of lime, by means of the oxyhydrogen blowpipe: after undergoing this operation it furnishes a ductile and malleable alloy of platinum with some of the metals which accompany it.

The alloy of platinum iridium and rhodium is well adapted to the preparation of crucibles, for if the proportions of the metals be properly adjusted, this alloy is harder and resists a higher temperature than pure platinum; at the same time it is less easily attacked by chemical agents. Such an alloy may be obtained from the crude platinum ore by simply fusing it by the oxyhydrogen blowpipe upon a bed of lime with a quantity of lime equal in weight to the amount of iron in the ore. Palladium and osmium are volatilized during this process of fusion, whilst the copper and iron become oxidized, and form fusible compounds with the lime.

(967) *Properties*.—Platinum is a white metal susceptible of a high lustre, and when pure is about as hard as copper. In ductility it rivals iron, and in tenacity it is inferior only to iron, cobalt, and nickel, and perhaps copper. It resists the highest heat of the forge; but it may be fused by the voltaic battery or by the oxyhydrogen blowpipe, before which it is volatilized, and is dispersed with scintillations. Deville and Debray state that it absorbs oxygen, and if melted in considerable masses spits like silver on rapid cooling. Attempts to crystallize platinum artificially have not succeeded, but very perfect octohedra have been met with in its native beds. Its specific gravity differs somewhat with the mode of manipulation to which it has been subjected, but it varies between 21 and 22, being (with the exception of iridium and osmium, which are equally dense) the heaviest form of matter as yet known. It expands less by heat than any other metal, and in its power of conducting heat and electricity it is much inferior to gold and silver,—in these respects ranking very near to iron.

Platinum does not undergo oxidation in air at any temperature: none of the acids have singly any effect upon it; aqua regia dissolves it, though but slowly. If heated to redness in air in contact with caustic alkalies or alkaline earths, especially with hydrate of lithia or with baryta, it is corroded, owing to the for-

mation of an oxide which combines with the alkaline base. When phosphorus is heated with spongy platinum, combination between them takes place readily. The attraction of sulphur for platinum is much less powerful. Dry chlorine is without action upon this metal, even when aided by heat.

(968) *Platinum black*.—Platinum may be obtained in a state of subdivision still finer than that in which it is left on heating the ammonio-platinic chloride. In this form it has the appearance of soot, and is termed *platinum black*. It may be procured in this condition by several methods, of which one of the most efficacious consists in dissolving platinous chloride in a strong solution of caustic potash, and adding alcohol to the hot liquid which is placed in a capacious vessel, and kept constantly stirred; brisk effervescence takes place, owing to the escape of carbonic acid; the platinum is reduced, and is deposited as a black powder, which requires repeated washing,—first with alcohol, next with potash, then with hydrochloric acid, and lastly with water. Platinum, in this finely divided state, greedily condenses oxygen from the air, and absorbs many times its bulk of the gas. If moistened with alcohol or ether it imparts this oxygen to them, and forms new compounds, whilst the powder glows from the heat which is extricated. In all its states, platinum possesses, in a marked degree, this property of condensing gases upon its surface; and the more finely it is divided, and consequently the larger the surface which it presents, the more striking is the phenomenon.

(969) *Uses*.—The most important applications of platinum are confined to the laboratory of the manufacturing and experimental chemist; they depend upon its great infusibility, and its power of resisting chemical agents. Its introduction as a material for the construction of apparatus employed by the analytical chemist has contributed in no small degree to the rapid progress of the science during the last forty or fifty years, by conferring upon its experiments a precision, neatness, and accuracy till then unattainable. In the concentration of oil of vitriol, large platinum stills are frequently employed; some of these vessels weigh upwards of 1000 ounces, or 28·4 kilos. It is found expedient to gild these vessels upon their inner surface, for, unless this precaution be adopted, the stills when made of platinum prepared by Wollaston's method, after a short time become sufficiently porous to allow the acid to transude. An attempt was made in Russia to employ platinum for coinage, but it was found to be inconvenient, and the experiment has been abandoned. Platinum is sometimes used for the touch-holes of fowling-pieces.

*Alloys*.—Platinum may be easily alloyed with many of the more fusible metals, the combination generally taking place with the extrication of light and heat. These alloys are much more fusible than pure platinum: care must therefore be taken not to heat the oxides of easily reduced metals, such as lead or bismuth, in platinum crucibles, as if the oxides should happen to be re-

duced, the crucible would be destroyed by the formation of a fusible alloy. Most of the platinum of commerce contains iridium, which, without impairing its power of resisting chemical agents, increases its hardness and durability. It is remarkable, that though pure platinum is perfectly insoluble in nitric acid, yet when alloyed with 10 or 12 times its weight of silver, both metals are easily and completely dissolved by the acid. An amalgam of platinum may be formed by acting upon an amalgam of sodium with a neutral solution of the sodio-platinic chloride ( $2\text{NaCl}, \text{PtCl}_2$ ); and, according to Level, when this amalgam is attacked by nitric acid, the platinum as well as the mercury is partially dissolved.

Platinum enters into combination with carbon and with silicon: sometimes in the fusion of ordinary platinum wire before the blowpipe, the globules of the melted metal become covered with a film of colourless glass, arising from the oxidation of the silicon and the fusion of the resulting silica. A brittle granular compound of platinum and silicon was accidentally obtained by Daniell, owing to the action of the silicon at a high temperature upon one of the platinum bars of his pyrometer. It appeared to be formed by a kind of cementation, the silicon being derived from the clay of the envelope in which the bar was heated: the proportion of silicon amounted to 1.5 per cent. A fusible compound of platinum with boron was also obtained by Wöhler and Deville.

(970) OXIDES OF PLATINUM.—There are two oxides of platinum, a protoxide and a dioxide. The *protoxide* (*platinous oxide*,  $\text{PtO}=213$ ) is procured by digesting platinous chloride in a solution of potash: a dark olive-green liquid is thus obtained, owing to the solution of the oxide in the excess of alkali. On neutralizing the solution with sulphuric acid, a black hydrated platinous oxide subsides. It is slowly dissolved by acids, forming unstable salts with them, and is readily decomposed by heat. Platinous sulphite forms several soluble double salts with the sulphites of the alkalis, such as  $2(3\text{K}_2\text{SO}_3, \text{PtSO}_3), 3\text{H}_2\text{O}$  obtained by heating potassio-platinous chloride with a solution of hydropotassic sulphite, when minute straw-yellow prisms are deposited on cooling. Similar salts exist with ammonium and silver.

The *dioxide*, or *platinic oxide* ( $\text{PtO}_2=229$ ), has a strong tendency to combine with alkaline bases; it is therefore prepared by adding to a solution of platinic nitrate only one half of the quantity of sodic carbonate which is necessary for its complete precipitation. It is thus procured as a voluminous brown hydrate ( $\text{PtO}_2, 2\text{H}_2\text{O}$ ), from which water is expelled at a gentle heat, whilst the mass becomes darker; a higher temperature expels the whole of the oxygen. Hydrated platinic oxide is soluble in solutions of potash and soda; the compounds thus formed may be obtained in crystals. The soda compound consists of  $\text{Na}_2\text{O}, 3\text{PtO}_2, 6\text{H}_2\text{O}$ . Platinic oxide also enters into combination with other bases, forming com-

pounds most of which are insoluble. This oxide is also soluble in acids, and forms well characterized salts, the solutions of which have a yellowish-brown colour.

(971) **SULPHIDES OF PLATINUM.**—Platinum combines with sulphur in two proportions,  $PtS$  and  $PtS_2$ .

*Platinous sulphide* ( $PtS$ ) may be obtained as a black precipitate by passing sulphuretted hydrogen over moistened platinous chloride; it may also be procured by heating sulphur with ammonio-platinic chloride, when it assumes the form of a grey powder of metallic appearance, from which the sulphur is completely expelled by heating it in the open air.

The *disulphide* ( $PtS_2$ ) is best procured by decomposing the sodio-platinic chloride by sulphuretted hydrogen; it falls as a dark-brown powder, which becomes black during desiccation. It is somewhat soluble in the sulphides of the alkali-metals. By ignition in closed vessels it is converted into protosulphide. When exposed to the air, and gently heated, it is partially converted into platinic sulphate, but at a higher temperature is wholly decomposed, metallic platinum remaining.

(972) **CHLORIDES OF PLATINUM.**—These correspond in number to the sulphides and oxides of the metal.

In order to procure the *platinous chloride*, formerly known as the *protochloride* ( $PtCl_2=268$ ), the solution of platinum in aqua regia should be evaporated, and the residue exposed to a heat of  $455^\circ$  ( $235^\circ$  C.), so long as any chlorine is expelled; the compound which remains is platinous chloride. It is of an olive colour, and is insoluble in water: it is scarcely acted upon by nitric or by sulphuric acid; hydrochloric acid dissolves it when warmed: and it is dissolved easily by caustic potash, and by platinic chloride, with which latter it forms a double salt, of so deep a brown colour as to appear opaque in a concentrated solution. It forms crystallizable double salts with the chlorides of the alkali-metals.

*Platinic chloride*, or *tetrachloride* ( $PtCl_4=339.1$ , formerly *bi-chloride of platinum*); *Comp. in 100 parts*, Pt, 58.11; Cl, 41.89.—This salt is obtained by dissolving platinum in aqua regia, and evaporating the solution to dryness by means of a steam heat.\* It is a deliquescent salt, and forms a deep orange-coloured solution in water, from which it may be obtained crystallized in prisms; it is also dissolved largely by alcohol and by ether.

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\* In an active laboratory a number of residues containing platinum gradually accumulate, and these may be turned to account in the following manner:—The solutions, mixed with the precipitates, are evaporated to dryness, and transferred to a clay crucible, in which they are heated strongly, with free access of air, in order to burn off organic matters; after which the residue is boiled with hydrochloric acid, then with water, and lastly with nitric acid; a thorough washing with water follows. The impurities having thus been removed, the residual platinum may be converted into tetrachloride by means of aqua regia.

When heated to  $455^{\circ}$  ( $235^{\circ}$  C.) it loses half its chlorine, forming platinous chloride, and if the temperature be further raised, it is completely decomposed, and metallic platinum is left. Platinic chloride may easily be reduced to a platinous salt by transmitting sulphurous acid through a boiling solution of the salt containing hydrochloric acid in excess; by excess of sulphurous acid the solution is slowly rendered colourless, when it contains platinous sulphite, and free hydrochloric acid.

With other chlorides, platinic chloride forms numerous double salts, which are produced by mixing the solutions of these chlorides with that of the tetrachloride, and evaporating. The *potassio-platinic chloride* ( $2\text{KCl}, \text{PtCl}_4 = 488.2$ ; *sp. gr.* 3.586) is a sparingly soluble anhydrous compound, which crystallizes in octohedra; it is insoluble in alcohol and in ether. This salt is commonly used as a means of determining analytically the quantity of potassium in a compound: 100 parts of this salt contain Pt, 40.37; K, 16.02 = as  $\text{K}_2\text{O}$ , 19.29. It is decomposed by a red heat, into potassic chloride and metallic platinum. The *sodio-platinic chloride* ( $2\text{NaCl}, \text{PtCl}_4, 6\text{H}_2\text{O}$ ), crystallizes in beautiful red striated prisms, which are soluble in water, alcohol, and ether. The *ammonio-platinic chloride* ( $2\text{H}_4\text{NCl}, \text{PtCl}_4 = 446$ ; *sp. gr.* 3.009) is very similar in appearance to the corresponding potassic salt, with which it is isomorphous: it is sparingly soluble in water, and is insoluble in alcohol and in ether. This salt is employed in analysis for determining the quantity of ammonia present in solutions; 100 parts of this salt contain, Pt, 44.17 and  $\text{H}_3\text{N}$ , 7.62. It is also made use of for separating platinum from the other metals with which it is associated, after they have been brought into solution by treating the ore with aqua regia (966). When ammonio-platinic chloride is ignited, the ammonium and chlorine are wholly expelled, and pure platinum remains in the spongy form.

(973) *Basic Ammoniacal Derivatives from the Chlorides of Platinum.*—The action of ammonia upon platinous chloride gives rise to the formation of several remarkable compound bases, the composition of which offers considerable interest in a theoretical point of view. Magnus found that if platinous chloride be dissolved in hydrochloric acid, the addition of an excess of ammonia to the boiling solution causes the deposition of brilliant, green, acicular crystals which are insoluble in water and in hydrochloric acid: they contain the elements of 1 atom of platinous chloride, and 2 of ammonia ( $\text{Pt}''\text{Cl}_2\text{H}_6\text{N}_2$ ). This compound, however, undergoes no change when digested at ordinary temperatures in solutions of the caustic alkalies, or in the concentrated acids, but when boiled with them it is slowly decomposed. If digested in diluted nitric acid, one-half of the platinum is separated as nitrate, and on evaporating the solution, a salt is obtained crystallized in small, brilliant flattened prisms ( $\text{PtCl}_2\text{H}_{10}\text{N}_2\cdot 2\text{HNO}_3$ ). Neither the chlorine nor the platinum can be detected in this solution by the usual tests. The nitric acid may be displaced from it by double decomposition

with sodic sulphate, phosphate, or oxalate, and a sparingly soluble sulphate, phosphate, or oxalate of the platinum base is then formed. The base of these salts (commonly called *Gros's salts*, from the name of their discoverer) has not been isolated.

Raewsky discovered that if the green salt of Magnus be boiled with concentrated nitric acid, red fumes are disengaged, and a different salt is formed, which may be obtained in crystals on evaporation. The nitric acid may be displaced from this compound by an equivalent quantity of oxalic or of carbonic acid.

Raewsky's nitrate may also, according to Hadow, be formed readily by boiling Gros's nitrate for some hours with a solution of argentic nitrate and nitric acid, by the following reaction;  $2(\text{PtCl}_2\text{H}_{10}\text{N}_4\text{HNO}_3) + 2\text{AgNO}_3 + \text{H}_2\text{O} = \text{Pt}_2\text{Cl}_4\text{H}_{20}\text{N}_8\text{O}_4\text{HNO}_3 + 2\text{AgCl} + 2\text{HNO}_3$ . A very characteristic reaction was obtained by Hadow with this salt, by giving with a very dilute solution of platinous chloride strongly acidulated with nitric acid, a beautiful copper-coloured moss-like precipitate.

Besides these compounds, other platinum bases derived from ammonia have been obtained, of which the following is a brief account:—

*Platosamine; Reiset's second base* ( $\text{Pt}''\text{H}_4\text{N}_3, \text{H}_2\text{O}$ ).—This is a greyish mass insoluble in water and in ammonia, which may be obtained by heating hydrated diplatosamine ( $\text{Pt}''\text{H}_{10}\text{N}_4, 2\text{H}_2\text{O}$ ) to  $230^\circ$  ( $110^\circ$  C.), so long as it gives off water and ammonia. It combines with acids, and forms salts, most of which are insoluble, and are decomposed on the application of heat. Platosamine dihydrochlorate ( $\text{Pt}''\text{H}_4\text{N}_3, 2\text{HCl}$ ) may be obtained by heating the dihydrochlorate of the following base, so long as it gives off water and ammonia.

*Diplatosamine; Reiset's first base* ( $\text{Pt}''\text{H}_{10}\text{N}_4, 2\text{H}_2\text{O}$ ).—This substance may be procured as a hydrate in deliquescent needles, which are powerfully alkaline, caustic, and absorb carbonic anhydride from the air. It is usually isolated by decomposing its sulphate by its exact equivalent of baric hydrate. In order to prepare its salts, Hadow recommends platinous chloride to be dissolved in warm moderately strong ammonia, filtered from any oxide of iron or iridium, and then concentrated by evaporation; a large crop of crystals of diplatosamine hydrochlorate is deposited on cooling, ( $\text{Pt}''\text{H}_{10}\text{N}_4, 2\text{HCl}, \text{H}_2\text{O}$ ). If a solution of this salt be decomposed with an equivalent of argentic sulphate, the diplatosamine sulphate is obtained, and may readily be procured in crystals; the nitrate may be obtained by the use of argentic nitrate. These salts are readily recognized by yielding a precipitate of the green compound of Magnus on the addition of a solution of platinous chloride. Hadow finds that the green compound of Magnus is but one of a series of double salts that diplatosamine hydrochlorate forms with other metallic chlorides, such as corrosive sublimate, and the chlorides of cadmium, palladium, tin and copper.

**Platinamine; Gerhardt's base** ( $\text{Pt}^{\text{iv}}\text{H}_2\text{N}_2\cdot 4\text{H}_2\text{O}$ ).—This compound may be obtained in the form of striated very brilliant rhomboidal prisms of a yellowish colour. It is nearly insoluble in boiling water, is not decomposed by a boiling solution of potash, but is readily dissolved by diluted acids, and forms a large number of crystallizable, sparingly soluble salts, which are of a yellowish colour. Some of these salts are neutral, and some are acid. Platinamine is usually obtained by adding ammonia to a boiling solution of the neutral nitrate. If platosamine dihydrochlorate be suspended in boiling water, and submitted to a current of chlorine, it combines with chlorine, and is slowly transformed into platinamine tetrahydrochlorate ( $\text{Pt}^{\text{iv}}\text{H}_2\text{N}_2\cdot 4\text{HCl}$ ), and this by long boiling with argentic nitrate is converted into basic platinamine nitrate ( $\text{Pt}^{\text{iv}}\text{H}_2\text{N}_2\cdot 2\text{HNO}_3\cdot 4\text{H}_2\text{O}$ ).

**Diplatinamine** is supposed by Gerhardt to be the base of the salts of Gros and of Raewsky; but it has not as yet been isolated.

The following table contains the formulæ of the principal series of these compounds which have been ascertained to exist:\*

1. Salts of <i>Platosamine</i> (Reiset's second base).					
Platosamine	...	...	...	...	$\text{Pt}^{\text{iv}}\text{H}_4\text{N}_2\cdot \text{H}_2\text{O}$
„ (yellow) hydrochlorate	...	...	...	...	$\text{Pt}^{\text{iv}}\text{H}_4\text{N}_2\cdot 2\text{HCl}$
„ nitrate	...	...	...	...	$\text{Pt}^{\text{iv}}\text{H}_4\text{N}_2\cdot 2\text{HNO}_3$
2. Salts of <i>Diplatosamine</i> (Reiset's first base).					
Diplatosamine (hydrated)	...	...	...	...	$\text{Pt}^{\text{iv}}\text{H}_{10}\text{N}_4\cdot 2\text{H}_2\text{O}$
„ hydrochlorate	...	...	...	...	$\text{Pt}^{\text{iv}}\text{H}_{10}\text{N}_4\cdot 2\text{HCl}\cdot \text{H}_2\text{O}$
Magnus's green salt	...	...	...	...	$\text{Pt}^{\text{iv}}\text{H}_{10}\text{N}_4\cdot 2\text{HCl}\cdot \text{Pt}^{\text{iv}}\text{Cl}_2$
Normal diplatosamine nitrate	...	...	...	...	$\text{Pt}^{\text{iv}}\text{H}_{10}\text{N}_4\cdot 2\text{HNO}_3$
Diplatosamine acid-carbonate	...	...	...	...	$\text{Pt}^{\text{iv}}\text{H}_{10}\text{N}_4\cdot 2\text{H}_2\text{CO}_3$
3. Salts of <i>Platinamine</i> (Gerhardt's base).					
Platinamine	...	...	...	...	$\text{Pt}^{\text{iv}}\text{H}_2\text{N}_2\cdot 4\text{H}_2\text{O}$
Normal platinamine hydrochlorate	...	...	...	...	$\text{Pt}^{\text{iv}}\text{H}_2\text{N}_2\cdot 4\text{HCl}$
Basic platinamine nitrate	...	...	...	...	$\text{Pt}^{\text{iv}}\text{H}_2\text{N}_2\cdot 2\text{HNO}_3\cdot 4\text{H}_2\text{O}$
Normal nitrate	...	...	...	...	$\text{Pt}^{\text{iv}}\text{H}_2\text{N}_2\cdot 4\text{HNO}_3$

\* The following papers may be consulted upon this subject: Gros, *Ann. de Chimie*, II. lxi. 204; Reiset, *Ib.* III. xi. 417; Raewsky, *Ib.* III. xxii. 278; Peyrone, *Liebig's Annal.* li. 1, and lv. 205; Gerhardt, *Comptes Rendus des Travaux de Chimie*, par Laurent et Gerhardt, 1849, p. 113, and 1850, p. 273; Buckton, *Q. J. Chem. Soc.* v. 213, and vii. 22; Hadow, *Journ. Chem. Soc.* 1866, 345.

These different bases may obviously be regarded as ammonias in which part of the hydrogen in one or in two atoms of ammonia has been displaced by *platinosum*,  $\text{Pt}^{\text{iv}}$ , or by *platinicum*,  $\text{Pt}^{\text{iv}}$ ; platosamine and platinamine being formed upon the type of two atoms of hydrated ammonia ( $\text{H}_6\text{N}_2\text{H}_2\text{O}$ ) and diplatosamine and diplatinamine upon that of 4 atoms ( $\text{H}_{12}\text{N}_4\text{H}_2\text{O}$ ), as will be rendered manifest by examining the formulæ given in the table.

4. *Salts of Diplatinamine.*

Diplatinamine (not isolated) ... ..	$\text{Pt}^{\text{IV}}\text{H}_8\text{N}_4, 2\text{H}_2\text{O}?$
„ hydrochlorate ... ..	$\text{Pt}^{\text{IV}}\text{H}_8\text{N}_4, 2\text{HCl}?$
Normal nitrate ... ..	$\text{Pt}^{\text{IV}}\text{H}_8\text{N}_4, 2\text{HNO}_3, 2\text{H}_2\text{O}$
Sesquinitrate ... ..	$\text{Pt}^{\text{IV}}\text{H}_8\text{N}_4, 3\text{HNO}_3, 2\text{H}_2\text{O}$

5. *Salts obtained by Gros.*

Base (not isolated) ... ..	$\text{Pt}^{\text{IV}}\text{Cl}_2\text{H}_{10}\text{N}_4, \text{H}_2\text{O}?$
Hydrochlorate* ... ..	$\text{Pt}^{\text{IV}}\text{H}_8\text{N}_4, 4\text{HCl}$
Nitrate* ... ..	$\text{Pt}^{\text{IV}}\text{H}_8\text{N}_4, 2\text{HCl}, 2\text{HNO}_3$

6. *Salts obtained by Raewsky.*

Nitrate (crystallized) ... ..	$\text{Pt}_2\text{Cl}_2\text{H}_{20}\text{N}_8\text{O}_4, 4\text{HNO}_3$
Carbonate ... ..	$\text{Pt}_2\text{Cl}_2\text{H}_{20}\text{N}_8\text{O}_4, 2\text{H}_2\text{CO}_3$

(974) The *Platinic bromide* ( $\text{PtBr}_4$ ) is a brown insoluble powder. *Platinic iodide* ( $\text{PtI}_4$ ).—On adding potassic iodide to a dilute solution of platinic chloride the liquid assumes a deep wine-red colour; the mixture remains clear at ordinary temperatures, but becomes turbid and deposits a brown sparingly soluble powder when heated.

*Fulminating platinum* ( $\text{Pt}^{\text{IV}}\text{H}_8\text{N}_4, 4\text{H}_2\text{O}?$ ) is procured as an insoluble black powder by dissolving the ammonio-platinic chloride ( $2\text{H}_4\text{NCl}, \text{PtCl}_4$ ) in a solution of caustic soda and adding an excess of acetic acid, or by precipitating the sulphate with an excess of ammonia. It may be regarded as hydrated diammonium oxide [ $(\text{H}_4\text{N})_2\text{O}, 2\text{H}_2\text{O}$ ] in which 4 atoms of hydrogen have been displaced by one atom of platinum. Hydrochloric acid dissolves this compound, forming with it a very soluble, uncrystallizable salt: other acids decompose it with formation of ammoniacal salts. If suddenly heated to about  $392^\circ$  ( $200^\circ \text{C.}$ ) it explodes.

*Platinic sulphate* may be formed by dissolving the platinic oxide in dilute sulphuric acid, or by treating the disulphide with fuming nitric acid, and heating, to expel the excess of nitric acid. *Platinic nitrate* may be formed by decomposing a solution of the sulphate by an equivalent quantity of baric nitrate; both these platinic salts yield insoluble double basic salts on the addition of an alkali.

(975) CHARACTERS OF THE SALTS OF PLATINUM.—I.—The *platinous salts* are unimportant.

2.—Of the *platinic salts* the tetrachloride is the only soluble compound of frequent occurrence. These salts are distinguished by the following characters. When heated they are all decomposed, and leave a residue of metallic platinum. They have a brownish-yellow colour in solution: with *caustic potash*, or with

\* Viewed by Gerhardt as diplatinamine perhydrochlorate and dichloronitrate.



any potassic salt, they give a yellow precipitate of potassio-platinic chloride, which is soluble in a large excess of caustic potash; *caustic soda* precipitates a brown hydrated dioxide which is soluble in excess of the alkali: with *ammonia*, or a soluble salt of ammonium, yellow ammonio-platinic chloride is precipitated, which is decomposed by heat, leaving metallic platinum. *Sulphuretted hydrogen* and *ammonic hydrosulphide* give a black sulphide, which is soluble in a large excess of the sulphides of ammonium and of the alkali-metals.

Solutions of the platinic salts are reduced by *mercurous nitrate*, but not by *ferrous sulphate*. *Stannous chloride* in acid solutions produces a very deep brown solution, but yields no precipitate; *potassic iodide* slowly gives a brown precipitate of platinic iodide which becomes more abundant when heated. The solutions of the platinic salts are readily reduced to the metallic state by means of *zinc* or *iron*. Oxalic acid exerts no reducing action upon the salts of platinum, which may thus be separated from those of gold; and after the gold has been precipitated in this manner, the platinum may be thrown down in the metallic form by boiling the liquid with a soluble formiate, taking care first to neutralize the liquid by the addition of sodic carbonate.

(976) *Estimation of Platinum*.—Platinum may be estimated either in the metallic state, or in the form of a double chloride of platinum with potassium or ammonium. The solutions from which these double salts are precipitated should be concentrated; the complete separation of the salt is favoured by the addition of alcohol; and the washing of the precipitate should be performed with dilute alcohol. Platinum may thus be separated from all the metals hitherto described: 100 parts of the potassio-platinic chloride contain 40·37 of the metal; and 100 parts of the ammoniacal double salt contain 44·17 of platinum.

§ V. PALLADIUM: ( $\text{Pd}'' = 106\cdot5$ .) *Sp. Gr.* from 11·4 to 11·8; usually *Dyad*; rarely *Tetrad*.

(977) PALLADIUM is one of the rare metals which occur chiefly in the ore of platinum, in which it was discovered by Wollaston, in the year 1803. It usually forms from a half per cent. to one per cent. of these ores. According to G. Rose, palladium is dimorphous, since it is found native in cubes, and in six-sided plates.

In order to extract the metal from the ore of platinum, the solution of this ore in aqua regia is treated with sal ammoniac with a view to separate the platinum, as already described (966), and to the filtered liquid, mercuric cyanide in solution is added;

a yellowish-white, flocculent palladious cyanide subsides; this is converted into a sulphide by heating it in contact with sulphur, and the sulphur is subsequently expelled by repeated roastings. Another source of palladium is the native alloy which it forms with gold, and which is found in the Brazilian mines. In order to extract the palladium from it, Mr. Cock directs the alloy to be fused with silver, and then boiled in nitric acid, by which all the metals except the gold are brought into solution. The decanted liquid is next mixed with a solution of common salt, by which the whole of the silver is thrown down in the form of chloride, while the palladium with the other metals (principally copper with some lead and iron), still remains dissolved. Bars of metallic zinc are then introduced into the liquid, and these metals are precipitated upon the zinc in the form of a black powder, consisting of reduced metal. This precipitate is washed and redissolved in nitric acid, supersaturated with ammonia, which dissolves the oxides of palladium and copper, while those of iron and lead are precipitated: the clear liquid is now supersaturated by hydrochloric acid. Palladium is thus thrown down in the form of a yellow, sparingly soluble palladamine hydrochlorate ( $\text{Pd}^{\text{IV}}\text{H}_6\text{N}_2\text{Cl}_2$ ); by ignition of this salt the palladium is reduced, and agglutinates, but does not fuse. A small quantity of palladium still remains in solution, and may be recovered by the introduction of bars of iron.

Palladium is a white hard metal possessed of considerable ductility and tenacity. It is not fusible in an ordinary wind furnace, but melts at a lower temperature than platinum. Deville and Debray state that, like silver, it absorbs oxygen when melted, and as the metal cools the globule spits. Before the oxyhydrogen blowpipe it burns with scintillation, and if heated on lime it is slowly dispersed in green vapours. It undergoes no change in the open air at ordinary temperatures; but at a low red heat it becomes covered with an iridescent film, owing to a superficial oxidation; on increasing the heat, the oxygen is expelled, and the metal resumes its brilliant surface. Palladium is dissolved when heated in nitric acid, or in aqua regia, but it is acted upon by the other acids with difficulty. When fused either with hydropotassic sulphate, with nitre, or with the hydrated alkalies, it is oxidized. If a solution of iodine in alcohol be evaporated on a slip of palladium, a stain is left, by which this metal is at once distinguished from platinum. Palladium combines readily with gold, which is rendered brittle by its presence even in small proportion. It has a remarkable power of whitening the colour of gold, even

though present in the mixture only in small quantity; and when it forms 20 per cent. of the mass, the alloy is quite white. If alloyed with twice its weight of silver it forms a ductile compound not liable to tarnish, and well adapted for the construction of small weights. When melted with 8 times its weight of tin, at a red heat, an alloy is formed ( $\text{Pd}_3\text{Sn}_8$ ), which is obtained in beautiful brilliant lamellæ on digesting the mass when cold in hydrochloric acid. Palladium has been applied in a few cases to the construction of graduated scales for astronomical instruments, for which, by its whiteness, hardness, and inalterability in air, it is well adapted.

(978) **OXIDES OF PALLADIUM.**—This metal appears to form three oxides: a suboxide,  $\text{Pd}_2\text{O}$ , which furnishes a series of salts resembling those of cupreous oxide, and which, according to Kane, is obtained by heating the hydrated protoxide to incipient redness; a protoxide,  $\text{PdO}$ , the base of the ordinary salts of the metal; and a dioxide,  $\text{PdO}_2$ .

The *protoxide, palladious oxide* ( $\text{PdO} = 122.5$ ), may be procured as a black powder, by heating the nitrate to low redness; or it may be obtained upon adding potassic or sodic carbonate to a palladious salt, as a dark brown hydrate, soluble both in acids and in alkalis, and from which the water may be expelled by heat. At a bright red heat it loses its oxygen.

The *dioxide, palladic oxide* ( $\text{PdO}_2$ ), is prepared by decomposing the solid potassio-palladic chloride ( $2\text{KCl}, \text{PdCl}_4$ ) by a solution of caustic potash; it forms a yellowish-brown hydrate, which obstinately retains a portion of alkali: it is soluble in the alkalis: by boiling it with water it is rendered anhydrous, and is then deposited as a black powder.

*Palladious sulphide* ( $\text{PdS}$ ) may be formed either directly, by heating powdered sulphur with palladium, or by precipitating a palladious salt by means of sulphuretted hydrogen; it forms a fusible, greyish-white, lustrous mass, from which patient roasting in air expels the sulphur.

If a piece of palladium foil or wire be held in the flame of a spirit-lamp, soot is speedily deposited in large quantity, the foil or wire is corroded, and the mass of soot is found to contain palladium throughout, owing to the formation of a carbide of the metal.

(979) *Palladious chloride, or Chloride of palladium* ( $\text{PdCl}_2$ ) is obtained by evaporating to dryness a solution of palladium in aqua regia; it forms brown hydrated crystals, which become black when the water is expelled; if heated to redness metallic palla-

dium is left. Palladious chloride forms double salts with the soluble chlorides; those with potassium and ammonium are dark bottle-green. With ammonia, palladious chloride forms a series of compounds analogous to those of platinum (973): by mixture of a moderately concentrated solution of palladious chloride with a slight excess of ammonia a flesh-red precipitate is formed, which at  $100^{\circ}\text{C.}$ , when moist, passes into a yellow isomeric compound. This latter contains a salt of *palladamine* ( $\text{PdH}_6\text{N}_2\text{O}$ ), which is a crystallizable powerfully alkaline base. *Palladic chloride* ( $\text{PdCl}_2$ ) exists in solution in aqua regia, but cannot be obtained in crystals: it forms double salts with the chlorides of the alkali-metals: the double salt with potassium ( $2\text{KCl}, \text{PdCl}_2$ ) crystallizes in ruby-red prisms.

*Palladious iodide*, or *Iodide of palladium* ( $\text{PdI}_2 = 360.5$ ); *Comp. in 100 parts*, Pd, 30.0; I, 70.0.—This compound is obtained by adding a solution of a salt of palladium in slight excess to one of potassic iodide. It is a black powder, insoluble in water, but soluble in ammonia, and in a solution of potassic iodide: a solution of palladious nitrate is sometimes employed as a precipitant for iodine when it is necessary to separate iodine from chlorine and bromine (541). Palladious iodide loses its iodine when strongly heated.

Cyanogen has a stronger attraction for palladium than for any other metal, so that a solution of a palladious salt will decompose one of mercuric cyanide. This *cyanide* ( $\text{PdCy}_2$ ) is procured as a yellowish precipitate by adding potassic or mercuric cyanide to neutral solutions of any of the palladious salts; it is soluble in ammonia, in acids, and in potassic cyanide; it forms a series of double cyanides.

*Palladious sulphate* ( $\text{PdSO}_4$ ) may be obtained by decomposing the nitrate by sulphuric acid, or by dissolving the oxide in sulphuric acid. It is a deliquescent salt which forms a deep brownish-red solution; when heated it loses acid, and furnishes a basic salt.

*Palladious nitrate* is formed by boiling nitric acid on palladium: it may be obtained in rhombic prisms; they are freely soluble in a small quantity of water, and yield a deep reddish-brown liquid; but on being largely diluted, the normal salt is decomposed, and an insoluble basic nitrate is precipitated. If ammonia in excess be added to the solution of the nitrate, an ammoniacal palladious nitrate may be crystallized from it in rectangular tables.

(980) CHARACTERS OF THE SALTS OF PALLADIUM.—Palladious

salts, or the ordinary salts of the metal, form either brown or red solutions, which when neutral are distinguished by the yellowish precipitate of palladious cyanide, formed on adding *mercuric cyanide*. The fixed *hydrated alkalies* precipitate palladious compounds in the form of a red or orange basic salt, which is soluble in excess of the alkali by the aid of heat. *Ammonia* and its *carbonate*, when added to a solution of palladious chloride, give a flesh-coloured precipitate, soluble in excess of ammonia. Palladious nitrate gives a brown precipitate with ammonia. *Potassic* and *sodic carbonates* yield a brown precipitate of the hydrated palladious oxide, with palladious salts. *Potassic iodide* precipitates a black palladious iodide. *Sulphuretted hydrogen* and *ammonic hydrosulphide* throw down a black palladious sulphide insoluble in the sulphides of the alkali-metals. Solutions of the salts of palladium are reduced by a solution of *ferrous sulphate*, and by many of the metals, the reduction being facilitated by heat. *Stannous chloride* produces a dark brown precipitate, soluble in hydrochloric acid, and forming an intensely green solution, which becomes reddish brown on dilution.

Palladium may be separated from all other metals, except copper and lead, by the addition of mercuric cyanide to the solution previously neutralized by means of sodic carbonate. Palladious cyanide when ignited in the air leaves metallic palladium.

§ VI. RHODIUM: ( $\text{Ro}''' = 104.3$ ). *Sp. Gr.* 12.1.

(981) RHODIUM was discovered by Wollaston in 1803. It usually forms about one-half per cent. of the ore of platinum; it may be extracted from the solution of this ore in aqua regia after the platinum and palladium have been separated by the addition of sal ammoniac and mercuric cyanide: the excess of the cyanide is next decomposed by acidulating the solution with hydrochloric acid, adding common salt, and evaporating to dryness: the sodic chloride then forms double chlorides with all the metals in solution; the residue is treated with alcohol (of sp. gr. 0.837), which dissolves all these double salts, except that of sodium and rhodium, which remains behind as a red powder: this is dissolved in water, and the rhodium thrown down in a pulverulent form by means of bars of metallic zinc. The sodio-rhodic chloride may also be decomposed by heating it in a current of hydrogen gas, when, on washing the mass with water, the rhodium is left in a pulverulent form.

Rhodium is a white, very hard metal; when quite pure, it is

malleable after fusion upon lime, and it then has a sp. gr. of 12.1. It requires a stronger heat to fuse it than platinum, and when melted has a similar tendency to absorb oxygen, and to spit as the globule sets.

Deville says that rhodium furnishes an alloy with platinum, which is easily worked; when the proportion of rhodium forms 30 per cent. or upwards of the alloy it is not attacked by aqua regia. When pure, rhodium is insoluble in the acids, though if alloyed in small quantity with platinum, copper, bismuth, or lead, it is dissolved with them in nitro-hydrochloric acid. Rhodium has a considerable attraction for oxygen, and may be oxidized by fusion with a mixture of nitre and potassic carbonate; hydropotassic sulphate also oxidizes the metal and forms a soluble potassio-rhodic sulphate ( $\text{KRo}_2\text{SO}_4$ ), while sulphurous anhydride escapes. If heated in contact with sodic chloride, in a current of chlorine, a soluble sodio-rhodic chloride ( $3\text{NaCl}, \text{RoCl}_3$ ) is produced.

(982) OXIDES OF RHODIUM.—Rhodium has a considerable attraction for oxygen: it appears to form two definite oxides,  $\text{RoO}$  and  $\text{Ro}_2\text{O}_3$ , besides some compounds intermediate between them. The *protoxide*, however, has not been obtained in a state of purity.

*Rhodic oxide*, or *Sesquioxide of rhodium* ( $\text{Ro}_2\text{O}_3 = 256.6$ ).—This is the only salifiable oxide of rhodium; it may be procured by heating rhodium with a mixture of nitre and potassic carbonate; the oxide forms an insoluble compound with potash, which is to be well washed, and decomposed by digestion with hydrochloric acid: the sesquioxide is thus left as a greenish-grey hydrate which is insoluble in all acids.

SULPHIDES.—Rhodium forms two sulphides,  $\text{RoS}$  and  $\text{Ro}_2\text{S}_3$ .

If the metal be heated in the vapour of sulphur, the two bodies unite with incandescence, and form the *protosulphide*, which has a bluish-grey colour, and fuses at a very high temperature; the sulphur burns off in the open air, and leaves a forgeable mass of metallic rhodium. The *sesquisulphide* may be obtained in the form of a brown hydrate by decomposing a hot solution of the sodio-rhodic chloride by means of potassic or sodic sulphide.

CHLORIDES OF RHODIUM.—Three of these, viz.,  $\text{RoCl}_3$ ;  $\text{Ro}_2\text{Cl}_5$ ; and  $\text{RoCl}_2$ , are stated by Berzelius to exist, but the last is the only one of importance.

*Rhodic chloride* ( $\text{RoCl}_3$ ), formerly called the *sesquichloride*, is formed by decomposing the potassio-rhodic chloride by silicofluoric acid, which separates the potassium as a gelatinous silicofluoride; the filtered liquid when evaporated to dryness leaves rhodic chlo-

ride. This chloride unites with many of the soluble chlorides to form crystallizable double salts, which are of a ruby or rose colour, whence the metal receives its name (from  $\rho\acute{o}\delta\omicron\nu$ , a rose): the sodium salt crystallizes in cubes or in octohedra, which are efflorescent in the air ( $3\text{NaCl}, \text{RoCl}_3, 9\text{H}_2\text{O}$ ); they are insoluble in alcohol. When rhodic chloride is supersaturated with ammonia, the precipitate formed at first is redissolved, and a characteristic yellow compound, consisting of  $(\text{RoCl}_3, 5\text{H}_3\text{N})$  is formed by boiling, and may be purified by evaporation and re-crystallization. This compound when ignited leaves pure rhodium in the form of a powder.

(983) CHARACTERS OF THE SALTS OF RHODIUM.—The sodiorhodic chloride is the best known of these compounds. The rhodic salts generally form rose-coloured solutions; they are decomposed by *iron* or *zinc*, which causes a deposit of metallic rhodium. Hydrated *potash* and *soda* slowly occasion a precipitate of yellow hydrated rhodic oxide, which retains a portion of the alkali obstinately; it is soluble in the excess of the alkali as well as in acids; if alcohol be added to the alkaline solution, a black precipitate occurs gradually without applying heat. *Potassic iodide* throws down a sparingly soluble yellow tri-iodide of rhodium. *Sulphuretted hydrogen*, when the solution is heated, slowly forms a brown precipitate insoluble in the alkaline sulphides. The *soluble sulphites* give a pale yellow precipitate. If the salts of rhodium be heated in a current of hydrogen, the metal is readily reduced: in this form it is insoluble in aqua regia, but if it be fused with hydropotassic sulphate, a double salt is formed which is soluble in water, with a pink colour.

#### § VII. RUTHENIUM: ( $\text{Ru} = 104.2$ ). *Sp. Gr.*, from 11 to 11.4.

(984) *Treatment of the Platinum residue.*—After the platinum ore has been exhausted with aqua regia, a residue is obtained which frequently contains both titaniferous iron and chrome iron; but its most important constituent is an alloy in flat plates or scales of a white colour and metallic lustre. This was formerly considered to be an alloy of osmium and iridium. It has, however, been found to consist of four metals—viz., osmium, iridium, ruthenium, and a small quantity of rhodium.

Fremy in separating the different metals contained in this residue avails himself of the oxidability of osmium and the volatility of its tetroxide. His process is the following:—About 200 grammes of the platinum residue placed in a porcelain or platinum

tube, and heated to redness, is roasted in a current of dry air; in the portion of the tube which projects from the furnace some fragments of porcelain are placed, and the tube is connected with a series of glass flasks for the purpose of condensing the tetroxide of osmium as it distils; in the last flask a solution of caustic potash is placed in order to retain such portions of the tetroxide as may have escaped condensation; and this flask is connected with an aspirator, by means of which a current of atmospheric air is maintained through the apparatus. The air is dried, and freed from organic particles before it enters the heated tube, by causing it to pass through tubes filled with pumice moistened with sulphuric acid. During the operation the osmium and ruthenium become oxidized; the tetroxide of osmium condenses in beautiful needles in the flasks, and mechanically carries forward the dioxide of ruthenium, which is deposited upon the fragments of porcelain in regular square prisms.\*

The fixed residue consists of an alloy of iridium and rhodium, mixed with a little osmium and ruthenium. This is to be fused with caustic potash, by which the oxide of ruthenium is removed and is dissolved out on washing the fused mass with water. The undissolved portion is ignited with four times its weight of nitre, and the product is treated with boiling water, which dissolves the osmium, and on cooling often deposits it in octohedral crystals as dipotassic osmite ( $K_2OsO_4 \cdot 2H_2O$ ). The residue now contains only iridic and rhodic sesquioxides in combination with potash. Aqua regia, when boiled upon it, converts most of the iridium into the soluble tetrachloride; a solution of potassic chloride is added to the liquid, after which crystals of potassio-iridic chloride ( $2KCl, IrCl_4$ ) are deposited as it cools. The rhodic oxide, which is left undissolved, since it is insoluble in aqua regia, is converted into a soluble double salt by mixing it intimately with an equal weight of sodic chloride, and heating the mass to dull redness in a current of dry chlorine.

(985) RUTHENIUM is a metal which, in 1845, was shown by Claus to exist in the ore of platinum. It is very hard, and brittle, and is scarcely fusible even before the oxyhydrogen blowpipe. The melted metal, according to Deville and Debray, has a sp. gr. of from 11 to 11.4. It absorbs oxygen at a red heat, and the

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\* Sometimes the osmide of iridium does not readily undergo oxidation. In such a case Deville fuses it with 8 or 10 times its weight of zinc, and heats it for some hours to full redness; he then dissolves out the zinc by hydrochloric acid, which leaves the platinum metals in the form of a fine black powder which is very easily oxidized in a current of air.



oxide so obtained is not decomposed by simple elevation of temperature. The metal is readily oxidized by fusion with nitre, or with caustic potash. Ruthenium accompanies the alloy of osmium and iridium in a proportion varying from 3 to 6 per cent.; but it is not found in the portion of platinum ore which is soluble in aqua regia. It is most easily obtained by Fremy's process (984). The dioxide of ruthenium is not volatile when heated alone, but is carried forward mechanically by the tetroxide of osmium, and becomes condensed in crystals near to the source of heat. By heating this oxide in a current of hydrogen, the metal is obtained in the form of a dark grey powder. The metal yields an alloy with tin,  $\text{RuSn}_3$ , which crystallizes in cubes of perfect regularity.

Ruthenium forms four compounds with oxygen,  $\text{RuO}$ ;  $\text{Ru}_2\text{O}_3$ ;  $\text{RuO}_2$ ; and  $\text{RuO}_3$ .

*Ruthenic anhydride*, or *Ruthenic acid* ( $\text{RuO}_3$ ), is insoluble in water: it may be obtained by heating any of the preceding oxides with nitre; dipotassic ruthenate is formed, and furnishes an orange-yellow solution in water. The *sesquioxide* is the most stable of the basic oxides of the metal; it is obtained in the anhydrous form by igniting the metal in a current of air. It is insoluble in the alkalis: but with acids it forms soluble salts which have a yellow colour. The alkalis precipitate the hydrated oxide ( $\text{Ru}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) from these solutions as a bulky blackish-brown powder.

There are three chlorides of ruthenium,  $\text{RuCl}_2$ ;  $\text{RuCl}_3$ ; and  $\text{RuCl}_4$ . The *trichloride* is obtained by dissolving the sesquioxide in hydrochloric acid: on evaporation it yields a greenish blue deliquescent mass, which is soluble in alcohol. *Sulphuretted hydrogen* causes a brown precipitate of ruthenic sesquisulphide in solutions of the trichloride, leaving a supernatant liquid of a fine blue colour, probably owing to the formation of a lower chloride of the metal; this reaction is very delicate, and characteristic of ruthenium. Metallic *zinc* also reduces the yellow trichloride to the blue dichloride, and ultimately precipitates the metal as a black powder. With *plumbic acetate* a purplish-red characteristic precipitate is formed. *Mercuric cyanide* renders the solution blue, whilst a blue precipitate is formed. The *caustic* and *carbonated alkalis* yield a black precipitate of the sesquioxide, insoluble in excess of the precipitant. *Sodic formiate* or *oxalate*, if boiled with salts of ruthenium, renders the solution colourless, but does not occasion any precipitate of reduced metal.

§ VIII. OSMIUM: (Os=199). *Sp. Gr.* 21·4.

(986) OSMIUM occurs associated with platinum in the form of an alloy of osmium, iridium, and ruthenium. It was discovered in the ore of platinum by Tennant, in 1803. Osmium may be obtained in the metallic condition by several processes. One of the simplest consists in treating volatile oxide of osmium ( $\text{OsO}_4$ ) obtained by Fremy's method (984) with hydrochloric acid and metallic mercury. Calomel is thus produced by the decomposition of mercurous oxide, which is formed at the expense of the oxygen contained in the oxide of osmium;  $\text{OsO}_4 + 8\text{Hg} + 8\text{HCl} = \text{Os} + 8\text{HgCl} + 4\text{H}_2\text{O}$ . The water and the superfluous acid are expelled by evaporation to dryness, and on heating the residue in a small porcelain retort, the excess of mercury and calomel is driven off, leaving pure osmium in a pulverulent form. In this finely divided state, it emits the odour of tetroxide of osmium, when exposed to a moist atmosphere; it takes fire when heated in the open air, and is dissolved by strong nitric acid, or by aqua regia, being converted into tetroxide of osmium. After ignition, however, it is no longer soluble in the acids. The specific gravity of osmium in the pulverulent form is about 10, but after it has been heated to the fusing-point of rhodium in the oxyhydrogen jet, it acquires a sp. gr. of 21·4. In order to obtain compact osmium, Deville and Debray oxidize the alloy of osmium and iridium by mixing it intimately with  $5\frac{1}{2}$  times its weight of baric dioxide, and heating it to a bright red for 2 hours, after which they distil with a mixture of eight parts of hydrochloric and one of nitric acid. The tetroxide of osmium which passes over is received into a solution of ammonia, supersaturated with sulphuretted hydrogen, and boiled. The tetrasulphide of osmium is separated by filtration, dried at a low temperature, placed in a crucible of gas-coke, which is enclosed in a clay crucible and luted down, then exposed for four or five hours to a heat sufficient to melt nickel. The osmium is reduced, and furnishes a brittle mass, the colour of which has more of a bluish cast than that of zinc. At a still higher temperature in the oxyhydrogen jet, at the fusing-point of rhodium, it becomes still denser. It may be heated in this condition to the fusing-point of zinc without emitting vapour, but it takes fire at a higher temperature. If heated with 7 or 8 times its weight of tin in a charcoal crucible to a full red heat, the osmium is dissolved by the tin, and crystallizes out on slow cooling. On treating the mass with hydrochloric acid, the osmium is left as a very hard

crystalline powder. It may also be combined with zinc, and on dissolving the zinc in hydrochloric acid the osmium is left as an amorphous combustible powder. Osmium appears to be the least fusible of the metals. In the oxyhydrogen jet platinum melts and is volatilized, and iridium and ruthenium undergo fusion, but osmium does not melt, though it is volatilized by the intense heat.

Osmium differs remarkably from the other metals of this group, and presents more analogy with arsenicum and antimony than with the noble metals.

(987) FIVE OXIDES OF OSMIUM are known:— $\text{OsO}$ ;  $\text{Os}_2\text{O}_3$ ;  $\text{OsO}_2$ ;  $\text{OsO}_3$ ;  $\text{OsO}_4$ . The anhydrous *protoxide* of osmium is of a grey-black, and insoluble in acids: its bluish-black hydrate is soluble in hydrochloric acid, forming a deep indigo-blue solution of the dichloride,  $\text{OsCl}_2$ , which absorbs oxygen rapidly, and becomes converted into the tetrachloride  $\text{OsCl}_4$ . The *sesquioxide* has not been isolated; it forms rose-red uncrystallizable salts. The *dioxide* is black. The *trioxide* possesses a feebly acid character; it cannot be isolated, but it forms a crystalline compound with potassium (*dipotassic osmite*,  $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$ ), which is sparingly soluble. This compound furnishes a good source of pure osmium. It is easily obtained by the addition of a little alcohol to a solution of the tetroxide of osmium in potash; the osmite separates in large rose-coloured octohedra, which are permanent in a dry air, but absorb oxygen if moist. If this salt be digested in a solution of ammoniac chloride, a yellow sparingly soluble salt is formed ( $2\text{H}_4\text{NCl} \cdot \text{OsO}_3 \cdot \text{H}_4\text{N}_2$ ), which, when ignited in a current of hydrogen, leaves pure osmium.

*Tetroxide of osmium*, formerly called *osmic acid* ( $\text{OsO}_4 = 263$ ; *Mol. vol.*   ; *rel. wt.* 131.5; *sp. gr. of vapour*, 8.88) is the volatile compound which is produced when the metal is heated with nitre, or when roasted in air: it forms colourless, acicular, transparent, flexible crystals which are readily fusible, and are freely soluble in water; it boils at about  $100^\circ \text{C}$ ., emitting an extremely irritating and deleterious vapour, with a pungent characteristic odour somewhat resembling that of chlorine: hence the name of the metal osmium (from  $\acute{o}\sigma\mu\eta$ , odour); this oxide does not combine with acids; but though it unites with the alkalis, its solution does not redden litmus, and its solutions in the alkalis give off the tetroxide when boiled. It produces a permanent black stain upon the skin when touched, owing to the partial reduction of the metal, and gives a characteristic blue precipitate when its solutions are mixed with tincture

of galls. According to Fremy, another oxide of osmium ( $\text{OsO}_5$ ?) exists, but it is very unstable; it forms compounds with potash and soda which have a dark-brown colour; they sometimes crystallize from concentrated alkaline solutions.

If the aqueous solution of tetroxide of osmium be treated with sulphuretted hydrogen, an immediate precipitate of the black hydrated *tetrasulphide* occurs, which is slightly soluble in solutions of the sulphides of the alkali-metals. Four inferior degrees of sulphuration of osmium also exist; they correspond in composition with the oxides. These sulphides are decomposed by prolonged ignition, and pure osmium is left.

(988) There are four *chlorides of osmium*, viz.— $\text{OsCl}_2$ ;  $\text{OsCl}_3$ ;  $\text{OsCl}_4$ ;  $\text{OsCl}_6$ : the *osmious dichloride*, ( $\text{OsCl}_2$ ) formerly the *protochloride*, is green, and sublimes in green needles; it is produced by heating powdered osmium in a current of chlorine; the double salts which it forms are of a green colour. The *osmic tetrachloride* ( $\text{OsCl}_4$ ), formerly the *bichloride*, is formed in the same way as osmious dichloride, but employing an excess of chlorine; it is more volatile, and condenses as a red, crystalline, fusible, deliquescent powder: both this and the preceding chloride are dissolved by water, which soon decomposes them, forming tetroxide of osmium and hydrochloric acid, and depositing metallic osmium. Osmic tetrachloride forms with potassic chloride a beautiful sparingly soluble red salt, which furnishes octohedral crystals ( $2\text{KCl}, \text{OsCl}_4$ ); this salt is obtained by heating a mixture of osmium with potassic chloride in a current of chlorine: it is isomorphous with the corresponding platinum salt, and yields a characteristic dark olive-green precipitate with argentic nitrate ( $2\text{AgCl}, \text{OsCl}_4$ ; Claus). Mercurous nitrate gives with it a reddish-brown precipitate: tannic acid gives with it, when heated, a dark-blue solution, and potassic ferrocyanide, a chrome-green liquid, passing into dark blue.

Double salts may also be formed which contain both osmious trichloride ( $\text{OsCl}_3$ ) and osmic hexachloride ( $\text{OsCl}_6$ ).

A compound of nitrogen, oxygen, and osmium ( $\text{Os}_3\text{N}_2\text{O}_4$ ?), was formed by Fritsche and Struve. It may be obtained by acting upon a mixture of caustic potash and ammonia by means of tetroxide of osmium: these chemists termed it *osman-osmic acid*. With the alkalies it forms yellow crystalline compounds, which detonate readily when they are struck or suddenly heated. The potassium salt may be represented by the formula,  $\text{K}_2\text{Os}_3\text{N}_2\text{O}_6$  (?).

The properties of the salts of osmium have been but incom-

pletely ascertained. When boiled with nitric acid they all evolve vapours of tetroxide of osmium.

§ IX. IRIIDIUM: ( $\text{Ir} = 197.1$ ). *Sp. Gr.* 21.15.

(989) IRIIDIUM was discovered at the same time as osmium, by Smithson Tennant. It is occasionally found native and nearly pure in considerable masses among the Uralian ores of platinum, but it usually occurs combined with osmium as an alloy in flat scales. Iridium appears to be dimorphous, for it is found crystallized both in cubes and in double six-sided pyramids (G. Rose). In order to obtain the metal in the separate state, Wöhler recommends the powdered alloy to be intimately mixed with an equal weight of finely powdered fused sodic chloride, and the mixture to be heated to dull redness in a glass tube through which a current of dry chlorine is transmitted so long as it is absorbed. The alloy is decomposed by the chlorine; double chlorides of iridium and sodium, and of osmium and sodium are thus formed. They are dissolved in boiling water, and are thus freed from the insoluble portions. The solution is then concentrated, and the liquid so obtained is mixed with nitric acid and distilled; the double salt of osmium is decomposed by this means, and tetroxide of osmium is formed, whilst the iridium salt remains in the liquid: the oxide of osmium being volatile, is expelled during the distillation. The addition of ammoniac chloride to the concentrated solution in the retort produces a precipitate of the ammonio-iridic chloride, which, upon ignition, yields metallic iridium. The metal, however, if obtained thus, is liable to be contaminated with ruthenium. It is preferable to adopt Fremy's method of procuring the potassio-iridic chloride (984). The salt may be decomposed by ignition in a current of hydrogen; and the potassic chloride may be removed by washing with water, when the iridium is left in the form of a finely divided powder.

Iridium is a very hard, white, brittle metal, which may be melted on lime by the oxyhydrogen blowpipe, or by the heat of the voltaic current. It was found to have in its fused condition a density of 21.15 (Deville and Debray); and a native alloy of platinum and iridium even of *sp. gr.* 22.6 is known. If heated in a finely divided state in the open air it absorbs oxygen, but if in mass it remains unchanged by exposure to heat. In its isolated form it is unacted on by any of the acids or by aqua regia; but when alloyed with platinum it is readily dissolved by aqua regia. Pulverulent iridium, when fused with nitre or with

the hydrated alkalies, becomes oxidized, and a similar effect is produced by heating it with hydropotassic sulphate. Iridium may be obtained in a finely divided state by decomposing a solution of its sulphate by alcohol: it then forms a black powder, which possesses properties similar to those of platinum black (968).

(990) OXIDES OF IRIIDIUM.—This metal forms three distinct combinations with oxygen,  $\text{IrO}$ ;  $\text{Ir}_2\text{O}_3$ ; and  $\text{IrO}_3$ : they pass readily one into the other, and thus give rise to the variety of tints which solutions of the salts of this metal assume. From these changes of colour the name iridium, derived from *Iris*, the rainbow, was conferred on the metal.

The *protoxide* is obtained as a black anhydrous powder by decomposing dry iridious dichloride ( $\text{IrCl}_2$ ) by means of a concentrated solution of potash. It is attacked by acids with difficulty, but is dissolved by the alkalies; the solution in caustic potash absorbs oxygen from the air, and becomes blue. Its solutions in the acids have a dingy green colour.

The *sesquioxide* is the compound formed when iridium is fused with hydrate of potash or with nitre, or by heating the pulverulent metal in air. It is a bluish-black powder, which is decomposed by a full red heat, and is readily reduced by hydrogen and combustible substances. This anhydrous oxide is insoluble in acids, and even in fused hydropotassic sulphate. If a solution of iridic trichloride be boiled with a solution of caustic potash, oxygen is absorbed, and an indigo-blue precipitate, which is a hydrated *iridious dioxide* ( $\text{IrO}_3 \cdot 2\text{H}_2\text{O}$ ), is formed (Claus). It may be rendered anhydrous by a gentle heat. The dioxide is but slowly dissolved by acids: the hydrochloric solution is at first blue, it then becomes green, and, when heated, changes to reddish-brown, whilst iridic tetrachloride is formed.

Three *sulphides* of iridium corresponding to the oxides may be prepared by decomposing the chlorides of the metal by means of sulphuretted hydrogen.

Iridium, like palladium, when held in the flame of a spirit-lamp, becomes covered with carbonaceous excrescences, which contain a considerable portion of metallic iridium.

(991) CHLORIDES OF IRIIDIUM.—These correspond in number with the oxides. They all form double salts with the chlorides of the alkali-metals. According to Claus, the *dichloride* ( $\text{IrCl}_2$ , formerly called the *protochloride*) may be obtained in solution in combination with potassic chloride, if the double salt of trichloride of iridium with chloride of potassium

( $3\text{KCl}, \text{IrCl}_3, 3\text{H}_2\text{O}$ ) be treated with a solution of the hydropotassic sulphite, until the green colour has passed into red; on evaporating the solution carefully, red crystals of the double salt ( $4\text{KCl}, \text{IrCl}_3 \cdot 2\text{K}_2\text{SO}_3, \text{IrSO}_3, 12\text{H}_2\text{O}$ ) are deposited. The *trichloride* ( $\text{IrCl}_3$ , the old *sesquichloride*) is the most stable of the three chlorides: it forms a solution of an olive-green colour; with mercurous nitrate it gives a bright ochre-yellow precipitate ( $\text{IrCl}_3, 3\text{HgCl}$ ), and a similar compound is formed with argentic nitrate which at first is dark-blue, but soon becomes colourless: it forms salts with sodic and potassic chloride. If dry chlorine be transmitted over a mixture of finely divided iridium and potassic chloride, a potassio-iridic chloride, of a reddish-black colour ( $2\text{KCl}, \text{IrCl}_4$ , *sp. gr.* 3.546), is formed. It may be dissolved in boiling water, and is deposited in anhydrous octohedra on evaporating the solution; it corresponds in composition to the yellow platinum salt, with which it is isomorphous. A similar salt of sodium may be formed in the same manner, by substituting sodic for potassic chloride: it is freely soluble. Iridic tetrachloride forms a similar salt with sal ammoniac, which possesses a very intense colouring power, and produces a dull brown solution even when much diluted. It is remarkable that the addition of caustic potash in small quantity to the tetrachloride converts it into the olive-green trichloride. Iridic tetrachloride, when heated with ammonia, forms a series of compound bases analogous to those furnished by platinum and palladium.

Claus considers that the compounds formerly described as containing trioxide and trichloride (hexachloride) of iridium were really compounds of ruthenium.

The salts of iridium have been but incompletely examined.

Iridium is apt to accompany the double chlorides of platinum with potassium and ammonium. It may be separated from platinum by precipitating the two metals together, by means of potassic chloride: the precipitate is washed, and either digested with potassic cyanide which dissolves the iridium and leaves the platinum; or it may be fused with twice its weight of potassic carbonate. The platinum is by the latter operation reduced to the metallic state, whilst the iridium remains in the form of sesquioxide. The potassium salts are removed by washing, and the platinum is redissolved by means of aqua regia, which does not attack the iridic sesquioxide. This operation sometimes requires repetition, as a portion of iridium may escape oxidation on the first occasion.

## CHAPTER XX.

ON SOME CIRCUMSTANCES WHICH MODIFY THE OPERATIONS OF  
CHEMICAL ATTRACTION.

(992) IN the first volume of this work an outline was given of the leading characters of the most important varieties of molecular and polar forces, as viewed in their simplest conditions. In the second volume the attention of the reader has hitherto been directed principally to the results produced by the exertion of chemical attraction in the formation of the various compounds of inorganic origin, without reference to the effects of other forces which may have concurred in their production. It will, however, now be advisable to trace the influence exerted upon the operation of chemical attraction by the co-operation or antagonism of elasticity and cohesion, of adhesion, and of heat. Cases in which the chemical decomposition of one substance by another is due simply to differences in the degree of chemical attraction are much less numerous than might at first be imagined. The displacement of one metal by another from its solutions, such as that of silver by mercury, of mercury by copper, of copper by lead, and of lead by zinc (7, ii.), furnishes some of the best examples of this kind; and similar instances are afforded by the displacement of one base by another insoluble base, as when cupric oxide is displaced from a solution of cupric nitrate by boiling it with freshly precipitated zincic oxide or with argentic oxide.

## § I. INFLUENCE OF COHESION, ADHESION, AND ELASTICITY.

(993) *Influence of Cohesion upon Chemical Attraction.*—Since chemical attraction is a molecular force which is exerted only when the particles of bodies are within distances indefinitely small, minute subdivision and diminution of cohesion might be expected to favour its manifestation, by increasing the surfaces, and facilitating the mutual contact of the combining bodies. It will therefore be needless to give more than one or two instances in proof of this point:—Iron, copper, lead, and many other metals, when exposed to the atmosphere in mass, are acted upon very slowly by it, and they become gradually converted into oxide upon the surface; if, however, they be reduced to a finely divided state, they are oxidized with such rapidity as often to become incandescent. If iron, cobalt, or nickel be reduced by hydrogen



from its oxide, at a low red heat, it is obtained in this form : by the interposition of some infusible matter between the particles of the precipitated oxide, as may be effected by precipitating a little alumina or magnesia along with the oxide, the tendency to rapid oxidation is much increased ; probably because the cohesion of the fine particles of reduced metal is mechanically prevented, and the access of the air to each portion takes place with facility. Copper, when precipitated from its solutions by metallic iron, or when reduced by means of hydrogen from its oxide at a low temperature, often takes fire and glows like tinder, when only a very slight elevation of temperature is applied to it. If a portion of plumbic tartrate be exposed in a glass tube to a heat sufficient to char the acid, the metallic lead is reduced throughout the mass in a state of extreme division, and when poured into the air it generally takes fire, and burns with scintillations.

The opposite influence, exercised by the force of cohesion, is seen on contrasting the facility with which disintegrated carbon burns when in the shape of tinder, with the difficulty which is experienced in effecting the combustion of the compact coke which is deposited from coal-gas upon the interior of the iron retorts ; and a decrease of combustibility may be traced through all the different forms of carbon, in proportion as their hardness and density increase.

(994) *Influence of Adhesion and Solution on Chemical Attraction.*—It is mainly to the intimate subdivision effected by means of solution, that this operation owes its important influence in facilitating chemical combination. The force of cohesion amongst the component particles of the bodies dissolved is balanced by their adhesion to those of the liquid, and the particles of the substance in solution, being free to move in any direction, easily obey the force of chemical attraction.

The influence of cohesion in preventing chemical action, and the manner in which the force of adhesion, as displayed in the production of solution, may act in favouring chemical action, are well exemplified by the effect of nitric acid upon baric carbonate. Baric nitrate, although soluble in water and in diluted nitric acid, is not soluble in the concentrated acid : when, therefore, concentrated nitric acid is poured upon finely powdered baric carbonate, it occasions but a slight effervescence, which speedily comes to an end, although the acid may be in large excess. If the liquid be diluted with a small quantity of water, a brisk effervescence is temporarily renewed, but again soon ceases ; on a further addition of water, a fresh effervescence occurs, and when the acid has been diluted

with 8 or 10 times its bulk of water, the whole of the baric carbonate is decomposed and dissolved.

For a similar reason, alcoholic solutions of acids are without action on the carbonates, unless the resulting salt be soluble in alcohol. A mixture of tartaric acid and alcohol will not decompose potassic carbonate. Hydrochloric acid when dissolved in alcohol will not decompose potassic carbonate, but will decompose calcic carbonate. An alcoholic solution of nitric acid decomposes calcic but not potassic carbonate. The tartrates are insoluble in alcohol, so are potassic chloride and nitrate, but calcic chloride and nitrate are dissolved by alcohol freely.

(995) *Influence of Elasticity*.—In the numerous instances in which two salts produce mutual decomposition, frequent examples are afforded of the results produced by the interference of other forces with that of chemical attraction. The action of ammoniac sulphate on calcic carbonate affords a case in point. If these two salts be mixed in a dry state, at ordinary temperatures, they do not appear to act upon each other; but if subjected to the influence of a gentle heat, a double decomposition occurs, ammoniac carbonate and calcic sulphate are produced; the volatile ammoniac carbonate is expelled, and by the aid of the force of elasticity, it is removed from the mixture;  $\text{CaCO}_3 + (\text{H}_4\text{N})_2\text{SO}_4$  yielding  $(\text{H}_4\text{N})_2\text{CO}_3 + \text{CaSO}_4$ . But suppose a solution of calcic sulphate to be mixed with one of ammoniac carbonate, the effects are exactly reversed; calcic carbonate, owing to its insolubility and the predominance of cohesion among its particles, is precipitated, whilst the soluble ammoniac sulphate remains in the liquid; and now  $(\text{H}_4\text{N})_2\text{CO}_3 + \text{CaSO}_4$  become  $\text{CaCO}_3 + (\text{H}_4\text{N})_2\text{SO}_4$ . The chemist very often avails himself of the influence of elasticity in promoting chemical decomposition. When, for example, an acid is added to a salt, it may decompose that salt, and its radicle take the place of the oxion or radicle previously in combination with the basyl, provided that the acid of the original salt can assume the gaseous form at ordinary temperatures, or can be converted into vapour at a temperature below that required to volatilize the acid employed to displace it. Carbonic acid may thus be displaced from the carbonates by solutions of all the ordinary mineral and vegetable acids, except the hydrocyanic and hydrosulphuric acids.

It is upon this principle that sulphuric acid, when aided by heat, is employed to displace the nitric, the hydrochloric, the acetic, the formic, the butyric, and other volatile acids from their metallic salts by distillation. Even a feeblor but more fixed acid

may expel the stronger acids which are more volatile than itself; oxalic acid, for example, if boiled with solutions of the chlorides, expels hydrochloric acid from the liquid with facility.

A remarkable illustration of the important influence exerted by elasticity in counteracting powerful chemical attractions, is afforded in the decomposition of the sulphates themselves, by weaker acids at a high temperature :—for example, the action of sulphuric acid upon bases is of the most energetic kind, whilst that of boracic acid, on the contrary, is extremely feeble. If a solution of borax be mixed with sulphuric acid, the sodium of the salt will change places with the hydrogen of the sulphuric acid as it is added, whilst boracic acid will gradually be separated, and if the liquid be hot and not too concentrated, will be retained in solution. Owing to the peculiar action of boracic acid on blue litmus, it can be shown that the two acids do not divide the sodium between them, for if a piece of blue litmus-paper be placed in the liquid, it will exhibit the peculiar wine-red tint due to boracic acid, until a quantity of sulphuric acid exactly equivalent to the sodium contained in the borax has been added; but the moment that this point is reached, the least excess of sulphuric acid immediately reveals itself by the change of the colour of the litmus from dusky purplish-red to a bright red. It is therefore clear that boracic acid cannot effect even a partial displacement of sulphurion from its combination with sodium when the two are in solution. But it is otherwise at a red heat: if boracic anhydride be fused with sodic sulphate, borax is produced, and sulphuric anhydride, which is volatile at this high temperature, is expelled in the elastic form. Other acids and anhydrides which are known to have a feebler attraction for bases than sulphuric acid, but which support a red heat without experiencing volatilization, such as the phosphoric and silicic anhydrides, are also able to decompose the sulphates when heated with them.

In like manner when a base which is fixed is heated with the salt of a volatile base, the volatile base is displaced by the more fixed one; thus quicklime or caustic potash, if heated with an ammonium salt, is converted into a calcic or potassic salt, whilst water and gaseous ammonia are expelled;  $2\text{H}_4\text{NCl} + \text{CaO} = \text{CaCl}_2 + \text{H}_2\text{O} + 2\text{H}_3\text{N}$ .

(996) The effect of elasticity in removing from the sphere of action one of the components of a body which is undergoing decomposition, may in some cases be considerably assisted by mechanical means; and when the attractions of the displacing body, and of the substance displaced by it, for the other constituent of

the compound, are nearly equal, effects which are in apparent opposition to each other may sometimes be produced. For instance, ferric oxide, when heated to redness in a current of hydrogen gas, is gradually reduced to the metallic state: the steps of the process appear to be these:—A small quantity of water is formed; it immediately diffuses itself in vapour into the hydrogen, and is mechanically carried away by the current of this gas, which must be employed in considerable excess for this purpose; and this process goes on until the reduction is complete. On the other hand, if metallic iron be heated in a current of steam, water is decomposed, hydrogen is liberated, and is carried beyond the reach of chemical action upon the newly formed oxide of iron by the excess of the steam employed. In a similar manner, if a current of sulphuretted hydrogen be transmitted in large excess over solid hydropotassic carbonate, aided by a gentle heat, carbonic anhydride and water will be displaced from the acid-carbonate, and carried forward by the excess of the gas, whilst dipotassic sulphide will be formed:  $2\text{KHCO}_3 + \text{H}_2\text{S} = 2\text{CO}_2 + 2\text{H}_2\text{O} + \text{K}_2\text{S}$ . But dipotassic sulphide, if dissolved in water, and subjected to a current of carbonic anhydride, will, in its turn, be gradually but completely decomposed; the sulphuretted hydrogen being carried away by the excess of carbonic anhydride, whilst hydropotassic carbonate is formed in the liquid:  $\text{K}_2\text{S} + 2\text{CO}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{S} + 2\text{KHCO}_3$ .

(997) If elasticity be prevented by mechanical means from exerting its influence in removing a body from contact with others for which it has an attraction, combinations may be obtained which cannot otherwise be procured. Wöhler (*Liebig's Annal.* lxxxv. 376) found that a hydrate of sulphuretted hydrogen may be obtained in colourless crystals, if a portion of persulphide of hydrogen, freed from acid, be sealed up in a strong glass tube with a small quantity of water; the persulphide gradually undergoes decomposition into crystallized sulphur and gaseous sulphuretted hydrogen, which, when liquefied in the absence of water, at ordinary temperatures, exerts a pressure of about 17 atmospheres. But if water be present, the gas combines with water, and forms a crystalline solid, which disappears with effervescence when the tube is heated to  $86^\circ$  ( $20^\circ \text{C.}$ ), but is reproduced on cooling. If a tube containing crystals of this compound be opened, the crystals immediately disappear with brisk effervescence. In other cases, the decomposition of compounds already formed may be retarded or prevented, by preventing the escape of the elastic constituent by mechanical means. Hydrate of chlorine offers an instance of this

kind. Under ordinary circumstances, this substance becomes liquid at a few degrees above the freezing-point of water, with escape of gaseous chlorine; but if the solid hydrate be sealed up in a glass tube, it remains solid even when the temperature rises as high as  $68^{\circ}$  ( $20^{\circ}$  C.), the pressure of chlorine within the tube retarding the decomposition. Again, calcic carbonate is decomposed in an open fire, at a red heat, into carbonic anhydride and quicklime; but if it be enclosed in an iron tube, the mouth of which is plugged to prevent the escape of the acid, the carbonate may be melted, and on cooling it furnishes a granular mass, which is still calcic carbonate, and has the appearance of marble (Sir J. Hall).

(998) *Action of Acids on Salts in Solution.*—Whenever an acid—that is to say, a salt of hydrogen—is added to the solution of a salt with the basyl of which the oxion or radicle of the added acid is capable of forming a soluble compound, it may be supposed to produce a partial exchange of its basic hydrogen with the basyl of the salt originally in solution, so that two acids and two salts may be present in the liquid, in some unknown proportions depending upon the strength of the relative attractions of the metal for the radicles of the two acids:—when, for example, potassic nitrate is mixed with sulphuric acid, part of the potassium may be supposed to exchange places with the hydrogen of the sulphuric acid, and part to remain united with the nitron, while a portion of nitric acid will be liberated, and will become mixed with the uncombined sulphuric acid: for example,  $2\text{H}_2\text{SO}_4 + 4\text{KNO}_3 = \text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + 2\text{HNO}_3 + 2\text{KNO}_3$ . The occurrence of such a decomposition as this, although probable, in many cases does not admit of direct proof. If an additional force be called into operation, such as the development of elasticity on the application of heat, the more volatile acid may be expelled in the form of vapour, and may thus be withdrawn from the sphere of action. This, however, is no proof that such an exchange of basyls actually existed before the heat was applied. In cases where the attraction of the radicle of one acid for the metallic basyl is very strong, while that of the other is feeble, the radicle of the stronger acid may (as in the case of sulphuric acid and borax, already cited) entirely appropriate the basyl to itself. But where the two acids at all approach each other in chemical power, it must be assumed that a partial exchange of the basyl for hydrogen takes place. Sometimes the occurrence of such a partition can be proved by the change of colour which ensues after the mixture has been effected. Cupric sulphate, for example, is of a blue colour when in solution, and cupric chloride is green. If a solution of the

blue sulphate be mixed with hydrochloric acid, it is evident that the copper enters partially into combination with the chlorine of the hydrochloric acid, since the solution assumes a bright green tint;  $2\text{CuSO}_4 + 4\text{HCl} = \text{CuSO}_4 + \text{CuCl}_2 + \text{H}_2\text{SO}_4 + 2\text{HCl}$ .

If the basyl form an insoluble compound with the radicle of the newly added acid, it is possible to decompose the original salt completely by its means. If, for instance, a solution of baric nitrate or acetate be mixed with sulphuric acid, it may be supposed that the barium divides itself between the two oxions in proportion to its attraction for each; but since baric sulphate is insoluble, it is at once withdrawn from the mixture, and the barium remaining in the original salt again divides itself between the two oxions; the fresh portion of baric sulphate, however, is immediately precipitated; and so, by a series of steps which, where the chemical attractions are strong, succeed each other far more rapidly than they can be described,—the whole of the barium is separated in the form of an insoluble sulphate, leaving the nitric or the acetic acid free in the solution.

A very feeble acid may even displace a more powerful one when the compound which it forms is insoluble in the menstruum in which it is suspended. Hydrocyanic acid will separate nitric acid from argentic nitrate, owing to the formation of the insoluble argentic cyanide;  $\text{AgNO}_3 + \text{HCy} = \text{HNO}_3 + \text{AgCy}$ . Tartaric acid will liberate sulphuric acid in a solution of argentic sulphate, owing to the formation of an insoluble argentic tartrate. Oxalic acid will precipitate cupric oxalate from a solution of cupric chloride; and Pelouze has observed that, if a current of carbonic anhydride be transmitted through a solution of potassic acetate dissolved in alcohol, acetic acid will be liberated, and potassic carbonate, which is insoluble in alcohol, will be separated; but no such change occurs in its aqueous solution, since potassic carbonate is freely soluble in water. This rule, however, is not without exception, where one acid is very powerful and the other is very feeble; calcic borate, for instance, is an insoluble salt, but a solution of boracic acid will not occasion any precipitate if mixed with one of calcic nitrate; calcic citrate and tartrate are also insoluble compounds, but neither solution of citric nor of tartaric acid occasions a precipitate in one of calcic nitrate.

In like manner, if the acid originally present be insoluble in water, it will be separated, and the salt will be decomposed; for example, on the addition of nitric acid to a solution of potassic tungstate, the tungstic acid is precipitated, whilst potassic nitrate is retained in the solution;  $2\text{HNO}_3 + \text{K}_2\text{WO}_4 = 2\text{KNO}_3 + \text{H}_2\text{WO}_4$ .

(999) *Action of Bases on Salts in Solution.*—An analogous decomposition occurs if a quantity of some additional base be added to a saline solution. If the two bases be soluble, and the salts which they form be also soluble, the solution will remain clear, and it may be supposed that the acid radicle is divided between the metals of the two bases in proportion to its attraction for each, as when a solution of baric nitrate is mixed with a solution of caustic potash: a mixture of baric and potassic nitrate with baric and potassic hydrate is thus obtained; but as baric hydrate is less soluble than potassic hydrate, a portion of baric hydrate will be gradually deposited if the solutions be in a concentrated form. If either of the bases be insoluble, or form an insoluble salt with the acid, a complete separation of the base or of the acid contained in the original salt may be effected. For example, the salts of nearly all the metals, with the exception of those of the alkalies and of the alkaline earths, are derived from metallic oxides which are not soluble in water: the addition of any soluble base, such as potash, soda, or ammonia to their solutions, immediately occasions the precipitation of the insoluble oxide. It is in this manner that such oxides are commonly prepared from their solutions; for example, the oxide of zinc, of iron, of cobalt, of nickel, of manganese, or of silver, may thus be completely separated from the acid by which it was previously held in solution; for instance,  $2\text{KHO} + \text{CoSO}_4 = \text{CoO}, \text{H}_2\text{O} + \text{K}_2\text{SO}_4$ . Solution of the hydrate either of baryta, of strontia, or of lime, acts in a similar manner, if the acid be one which, like the nitric or the hydrochloric, is capable of furnishing a soluble compound by its action upon these bases. A solution of cupric nitrate may thus be decomposed by a solution of baric hydrate;  $\text{Cu}_2\text{NO}_3 + \text{BaO}, \text{H}_2\text{O} = \text{Ba}_2\text{NO}_3 + \text{CuO}, \text{H}_2\text{O}$ .

In a few cases, no precipitation occurs even though the oxide be insoluble; when, for instance, mercuric cyanide is mixed with a solution of potash, no precipitate is produced, although mercuric oxide is insoluble in water.

If the newly added base form an insoluble compound with the acid, it is wholly precipitated by it; and if the other base be soluble, it remains in the liquid. One of the methods of forming a pure solution of potash is founded on this principle; in this experiment, a solution of potassic sulphate is mixed with a quantity of solution of baric hydrate exactly sufficient to precipitate the whole of the sulphuric acid;  $\text{BaO}, \text{H}_2\text{O} + \text{K}_2\text{SO}_4 = 2\text{KHO} + \text{BaSO}_4$ ; and in a similar manner potassic oxalate is deprived of its oxalic acid by the addition of lime-water to its solution, owing to the

formation of an insoluble calcic oxalate. If the base as well as the salt which is formed by the addition of the new base to the acid be insoluble, it is possible to precipitate the whole of both acid and base from the liquid simultaneously; as when a solution of baric hydrate is added in regulated quantities to a solution of argentic sulphate;  $\text{BaO}, \text{H}_2\text{O} + \text{Ag}_2\text{SO}_4 = \text{Ag}_2\text{O}, \text{H}_2\text{O} + \text{BaSO}_4$ .

(1000) *Mutual Action of Salts in Solution.*—It is a rule almost without exception,\* *that when solutions of two salts, capable of forming, by interchange of their acid radicles and basyls, an insoluble or sparingly soluble salt, are mixed, the salts decompose each other, and the compound which is least soluble is precipitated.* It is in this manner that the greater number of insoluble compounds are formed by the process of double decomposition. Argentic iodide is thus obtained by acting upon a solution of argentic nitrate with one of potassic iodide;  $\text{AgNO}_3 + \text{KI} = \text{KNO}_3 + \text{AgI}$ ; and in a similar manner, if manganous carbonate or tricupric diphosphate be required, it may be procured by mixing a solution of manganous chloride or of cupric sulphate with one of potassic carbonate or of hydrodisodic phosphate. Sometimes a soluble compound may be advantageously procured in this manner, as in the ordinary method of preparing aluminic acetate, in which a solution of plumbic acetate is mixed with one of aluminic sulphate: plumbic sulphate is precipitated, and aluminic acetate remains dissolved;  $3(\text{Pb}_2\text{C}_2\text{H}_3\text{O}_2) + \text{Al}_2\text{SO}_4 = 3\text{PbSO}_4 + 2(\text{Al}_3\text{C}_2\text{H}_3\text{O}_2)$ .

When two saline solutions are mixed, which, by the interchange of their acid radicles and basyls, form compounds also freely soluble, there is in ordinary cases no proof that any change occurs, though it is usually supposed that a mixture of four different salts is produced. When, for instance, solutions of potassic sulphate and sodic nitrate are mingled, it is imagined that a mixture of potassic and sodic sulphates, and of potassic and sodic nitrates, in unknown proportion, dependent upon the balance of the mutual attraction of the oxions and basyls, is the result. In like manner the mixture of three salts, each containing a different radicle and a different basyl, would occasion the formation of nine different salts; and the mixture of four salts, each containing different oxions and different basyls, should produce sixteen

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\* When a solution of mercuric cyanide is mixed with one of argentic nitrate, little or no precipitate is produced, although argentic cyanide is a very insoluble compound, and mercuric cyanide has not the power of forming a soluble double cyanide with it.



different salts, provided that all are capable of coexisting in solution.

Hence it will be seen that it is impossible to state with certainty what are the salts which are present in mixture in any solution which contains a number of saline compounds. In the analysis of a mineral water, for example, it is possible to determine the amount of each acid radicle and of each basyl which is present, but it is not possible to say what the salts really were which were brought into solution to form the mineral water in question. Sulphion, nitron, carbion, and chlorine may have been present amongst the acid radicles, and potassium, sodium, calcium, and magnesium amongst the basyls; but it is impossible to say how all those radicles and basyls are distributed in the solution. Many chemists allot the basyls to the acid radicles in the order of the insolubility of the different salts, whilst others allot the strongest basyls to the strongest radicles. In reporting the results of analysis, however, the quantities of the separate salt radicles and basyls should invariably be given; in addition to which, the analyst, if he pleases, can allot them according to his fancy. The foregoing remarks may be illustrated by the curious alternate decompositions which differences of solubility at different temperatures sometimes bring about: a striking instance of this kind occurs in the case of a mixture containing both magnesian sulphate and common salt. These salts occur mixed together on a large scale in the mother-liquor of sea-water, after the bay-salt has been separated. Four salts may be formed by the intermixture of these two compounds, viz., magnesian sulphate, sodic sulphate, magnesian chloride, and sodic chloride. Of these four salts, sodic chloride is the least soluble at the boiling-point; if, therefore, the solution be concentrated by ebullition, sodic chloride is separated in crystals; and as the liquid cools, the magnesian sulphate crystallizes out. The effect, however, will be different if the solution be allowed to evaporate spontaneously in the open air; at low temperatures the sodic sulphate is the least soluble of the four salts; and at low temperatures it is the sodic sulphate which separates in crystals from the liquid, whilst the readily soluble magnesian chloride remains in solution (p. 406).

Upon a similar principle sodic nitrate is converted on a large scale into potassic nitrate, by mixing it with potassic chloride; on concentrating the solution by boiling it, sodic chloride is separated in crystals, and potassic nitrate crystallizes out as the liquid cools: at low temperatures sodic chloride is more soluble

than potassic nitrate, and the nitre crystallizes out nearly in a state of purity.

It may, in fact, be stated as a general principle, that on concentrating a mixed solution by evaporation, the salt which is least soluble at the particular temperature employed is that which is first formed.

In certain cases where there is no great difference in the solubility of two salts, evidence is yet afforded of their mutual decomposition when the solutions are mixed, by the change of colour which then ensues. Potassic sulphocyanide, for example, when mixed with a solution of ferric chloride, so much diluted as to be colourless, indicates by the blood-red solution which it forms, that a mutual interchange of the components of the two salts has been partially effected. In a manner somewhat similar, when a solution of ferrous sulphate is mixed with one of sodic acetate, on transmitting a current of sulphuretted hydrogen through the liquid, the iron is precipitated in the form of a black sulphide. This reaction could only take place owing to the presence of ferrous acetate, since a solution of ferrous acetate admits of being thus decomposed by sulphuretted hydrogen, but one of ferrous sulphate is not so acted upon. The entire quantity of iron may be separated in this manner, for no sooner is a certain proportion of the iron rendered insoluble, than a fresh portion of ferrous acetate is formed; and this formation and decomposition of the salt continues so long as any iron remains in a state of solution.

(1001) *Influence of Mass in the Formation of Chemical Compounds.*—A curious question presents itself as to the proportion in which two bodies are capable of thus decomposing each other on mixture. When, for example, three different bodies, A, B, and C, are mixed together, one of which, C, is capable of combining with either of the other two, and forming with them compounds, A C, B C, which in both cases are soluble, the quantity of A and of B being considerably in excess of C,—will the proportion in which C enters into combination with A and B, be determined merely by the strength of their relative chemical attraction? or will the proportion in which each of these bodies is present also influence the result? It was argued by Berthollet, that not only would C be divided between A and B, but that in proportion as the quantity of one of these bodies, A, preponderated over the other body, B, the proportion of A C in the mixture would be increased, while, of course, that of B C would be diminished. If, on the other hand, the proportion of B were increased, the quantity of the

compound  $B\ C$  would be augmented, whilst that of  $A\ C$  would be proportionately lessened, the body  $c$  dividing itself between  $A$  and  $B$ , in a proportion represented by the product of its chemical attraction for each of these elements multiplied into their mass. Thus if  $a$  represent the mass of  $A$ , let  $x$  represent its chemical attraction for  $c$ ; if  $\beta$  be the mass of  $B$ , and  $y$  its chemical attraction for  $c$ ; then  $ax : \beta y :: A\ C : B\ C$ . Suppose, for example, a solution of potassic nitrate to be mixed with more than its equivalent of sulphuric acid; it is generally conceded that the potassium divides itself between the two acids, forming a mixture of potassic sulphate and nitrate, with free sulphuric and nitric acids. Now if the quantity of sulphuric acid be increased, will the quantity of potassic sulphate which is thus formed be influenced by the amount of sulphuric acid which is thus added in excess? and if so, to what extent will this influence of the *mass* of the acid modify the simple effect of chemical attraction.

Let us imagine, for example, that  $x$ , the attraction of sulphion for potassium, = 5, whilst  $y$ , that of nitron for potassium, = 4. When an equivalent of sulphuric acid is presented to an equivalent of potassic nitrate, the mass  $a$  of sulphuric acid = 1: that of the nitric acid  $\beta$  = 1 also. Then  $ax : \beta y$  as 5 : 4. The nitrate will be partially decomposed:  $\frac{5}{9}$  of the potassium will enter into combination with the sulphion, whilst  $\frac{4}{9}$  will be united with nitron, and we shall have in the solution  $\frac{5}{9}$  ( $K_2SO_4$ ),  $\frac{4}{9}$  ( $2KNO_3$ ),  $\frac{1}{9}$  ( $H_2SO_4$ ) and  $\frac{5}{9}$  ( $2HNO_3$ ). But suppose, instead of adding 1 equivalent of sulphuric acid, 2 equivalents be employed, whilst the proportion of the nitrate remains unaltered; the mass  $a$  of the sulphuric acid is now 2, and  $ax : \beta y$  as 10 : 4. The proportion of potassic nitrate will be diminished, and there will be  $\frac{10}{14}$  ( $K_2SO_4$ ),  $\frac{4}{14}$  ( $2KNO_3$ ),  $\frac{1}{14}$  ( $H_2SO_4$ ), and  $\frac{10}{14}$  ( $2HNO_3$ ); and if 3 equivalents of sulphuric acid be employed to 1 of potassic nitrate, since the mass  $a$  of sulphuric acid is now = 3;  $ax : \beta y$  as 15 : 4; consequently the proportions of the ingredients would be  $\frac{15}{19}$  ( $K_2SO_4$ ),  $\frac{4}{19}$  ( $2KNO_3$ ),  $\frac{2}{19}$  ( $H_2SO_4$ ), and  $\frac{15}{19}$  ( $2HNO_3$ ); the proportion of potassic sulphate continuing to increase, though in a decreasing ratio, for every addition of free sulphuric acid to the solution.

(1002) *Gladstone's Experiments on Mass*.—No experimental solution of this problem was given by Berthollet, and the question fell into abeyance; but within the last few years several attempts have been made with considerable success to determine this question quantitatively. Gladstone (*Phil. Trans.* 1855, p. 179) has published a series of experiments in which he has made use of the change of colour which solutions of certain salts undergo on mix-

ture with each other, as a means of ascertaining the extent to which this mutual decomposition proceeds when all the products remain in solution. The principle of his experiments will be easily understood. Solutions of several ferric salts, such as the ferric sulphate, nitrate, chloride, acetate, citrate, &c., were prepared in such a manner that each should contain the same proportion of iron dissolved in the same bulk of water (each of the solutions employed contained a quantity of iron corresponding very nearly to 1 part of ferric oxide in 1000 parts of water). A solution of pure potassic sulphocyanide was then prepared of such a strength, that when 1 measure of this solution and 4 of that of the ferric salts were mingled, the proportion of sulphocyanogen should be exactly sufficient to convert the whole of the iron into sulphocyanide, if complete mutual decomposition occurred: thus the proportions of the two salts employed were such that it would be possible for exact mutual interchange to occur as represented in the following equation:  $\text{Fe}_26\text{NO}_3 + 6\text{KScy} = \text{Fe}_2\text{Scy}_6 + 6\text{KNO}_3$ . On making the experiment in this manner, it was found that the iron was never wholly converted into the red salt, for the tint was deepened by the addition of more either of the ferric salt or of the sulphocyanide. In order to obtain a quantitative estimate of the amount of these effects, definite measures of the solutions of ferric nitrate and of potassic sulphocyanide were mixed together, and the liquid so obtained was diluted with water until it occupied a known, but arbitrary volume. This diluted mixture furnished a liquid of a certain depth of colour which was employed as a standard of comparison. Another measure of the solution of ferric nitrate, equal to that used in the standard solution, was mixed with regulated additions of the potassic sulphocyanide, and the liquid thus obtained was diluted with measured quantities of water after each addition of sulphocyanide, until, as far as the eye could distinguish, this solution had the same depth of tint as that employed as the standard; it was then assumed that the quantity of ferric sulphocyanide formed was proportionate to the bulk of the two solutions.\* Suppose that the standard solution occupied a volume of 880 measures: it was found that if twice the quantity of the potassic sulphocyanide employed in the standard liquid were made use of in the new solution, this mixture would require dilution till it occupied 1270

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\* Gladstone found that simple dilution of the ferric sulphocyanide reduced the tint in a proportion greater than could be accounted for by mere dilution; but this source of error was eliminated, and was not found to present itself in other cases which he employed to test the accuracy of the general conclusion.

measures. The proportion of ferric sulphocyanide formed in these two cases was assumed to be as 880 to 1270, or as 1 to 1'44. The excess of sulphocyanide thus employed had therefore withdrawn an additional quantity of iron from its combination with the nitric acid.

In this manner experiments were made with quantities of the potassic sulphocyanide, progressively increasing from one-fifth of an equivalent of the sulphocyanide to each equivalent of ferric nitrate, up to 375 equivalents of sulphocyanide to 1 equivalent of ferric nitrate, and it was found that the quantity of ferric sulphocyanide which was formed, continued to increase with every addition of potassic sulphocyanide, though the effect of each consecutive addition became less and less marked.

It was ascertained, as indeed it was to be expected, that the proportions of ferric sulphocyanide, which are formed by the mixture of equivalent quantities of other salts of iron with given amounts of the potassic sulphocyanide, vary with the nature of the acid radicle contained in the ferric salt. For example, it was found that when ferric nitrate was mixed with potassic sulphocyanide, in the proportion of equivalent quantities of each, that 0'194 of an equivalent of the red salt was formed. When an equivalent of ferric chloride was used, 0'173 of an equivalent was formed; when ferric sulphate was employed, 0'126 of an equivalent was produced; with ferric acetate 0'04 only was formed; and when ferric citrate was employed, the quantity of ferric sulphocyanide which it yielded was too small to admit of being estimated. The iron therefore retained the radicles of these different acids with degrees of force which vary inversely with the quantity of ferric sulphocyanide which is formed, whilst the potassium in the sulphocyanide attracted them with a power in direct proportion to these quantities. Various attempts have been made to obtain relative numerical expressions for the force of chemical attraction by which different compounds are united, but they have all hitherto failed. Experiments conducted upon the principle of those of Gladstone appear to offer the fairest prospect of solving this interesting and important problem.

Besides the ferric sulphocyanide, Gladstone examined a variety of other coloured compounds; one of these was the scarlet auric bromide, which becomes yellow when mixed with potassic and sodic chlorides, to an extent varying with the proportion in which these salts are added: quinia sulphate, when mixed with a soluble chloride, bromide, or iodide, also afforded similar indications, as it loses its fluorescent character (110) in proportion to

the quantity of chloride or bromide with which it is mixed. From these and from a variety of other experiments, it appears that when two or more compounds in solution are made to act upon each other, provided that the products which they form by their mutual action are also soluble, the following conclusions may be drawn:—1. That mutual interchange between the bodies which are mixed takes place in determinate proportions. 2. That these proportions are independent of the manner in which the compounds were originally combined: thus, if potassic sulphate and ferric nitrate be mixed in equivalent quantities, the result is the same as if potassic nitrate and ferric sulphate had been employed in equivalent quantities. 3. That these proportions are dependent partly upon the strength of the mutual attractions of the components for each other, and partly also upon the *mass*, or relative proportion of each compound which is present in the mixture. 4. That the alteration of the mass of any one of these compounds alters the amount of all the other compounds which co-exist in the mixture, in a regularly progressive ratio; and these quantities admit of being represented by regular curves. In most cases this adjustment of the relative quantities of the different bodies takes place immediately that the mixture is made.

(1003) *Experiments of Bunsen and of Debus*.—The results are different if the products of the chemical combination be at once removed from the sphere of action,—as by the formation of gaseous compounds, or of an insoluble precipitate when two liquids are mixed. Bunsen has investigated the results obtained in some cases of gaseous combination. He found that when a mixture of hydrogen and carbonic oxide was detonated with oxygen in quantity insufficient for its complete combustion, the oxygen divided itself between the two gases in such a manner that the quantities of water and of carbonic anhydride produced were in very simple atomic relations to each other (*Liebig's Annal.* lxxxv. 137). He exploded together mixtures of oxygen, hydrogen, and carbonic oxide, in varying proportions, the hydrogen and carbonic oxide being each in considerable excess over the oxygen: under such circumstances water and carbonic anhydride were formed; but the quantity of carbonic anhydride was greater, in proportion as the carbonic oxide preponderated, according to a certain law. Similar results were obtained by detonating cyanogen with a quantity of oxygen insufficient for its complete combustion; in such case nitrogen and a mixture of carbonic anhydride and carbonic oxide in simple proportions were obtained: and when a mixture of carbonic anhydride and hydrogen was detonated with

a quantity of oxygen insufficient for the consumption of the hydrogen, a certain proportion of the carbonic anhydride was reduced to carbonic oxide, according to the terms of the same law.

The following is the law deduced by Bunsen from his experiments:—1. When two gaseous bodies, A, B, are mixed with a third body, c, and fired by means of the electric spark, the body c takes from A and B quantities which always stand to one another in a simple atomic relation: so that for 1 atom of A c, 1, 2, 3 or 4 atoms of B c are produced; for 2 atoms of A c, 3, or 5, or 7 atoms of B c are formed. If 1 atom of the compound A c, and one of B c be formed in this manner, the mass of A may be increased in the presence of B, up to a certain point, without any change in that atomic proportion; but if a certain limit be passed, the relation of atoms, instead of being as 1 : 1, suddenly becomes as 1 : 2, or as 2 : 3; and so on.

2. When a body, A, acting upon an excess of any compound, B c, reduces it, so that A c is formed, and B is set at liberty; then—if B in its turn can reduce the newly-formed compound, A c—the final result is, that the reduced part of A c is in simple atomic proportion to the unreduced part. In the case of these reductions also, the mass of one of the ingredients of the mixture may be increased up to a certain point without altering the relative proportions of the compounds obtained; but if increased beyond this limit, a sudden alteration in the relative proportions of the products occurs; but these proportions still admit of being represented by simple ratios. This second portion of the law needs confirmation by more extended experiments.

The following experiments illustrate the first part of the foregoing law:—On exploding mixtures of carbonic oxide and hydrogen with oxygen, in the following proportions, Bunsen found that the quantities of carbonic oxide and hydrogen which were oxidized were in the proportions stated below:—

		Oxygen.	Mixture detonated.		Carb. oxide.	Ratio of gases burned.		
			Hydrogen.			Hydrogen.	Carb. oxide.	
I.	...	10	...	20	...	79'4	...	1 : 2
II.	...	10	...	20	...	44'4	...	2 : 2
III.	...	10	...	20	...	12'1	...	6 : 2
IV.	...	10	...	37	...	31'5	...	8 : 2

These experiments show that, as the proportion of carbonic oxide to the hydrogen in the mixture decreased, the proportion oxidized on detonation decreased also, but it decreased *per saltum*, not gradually, and these proportions were found to be uniformly

the same on repeating the detonation with the same mixture, although the degree of compression to which the mixture was subjected during the detonation was considerably varied in different experiments.

The following are Bunsen's principal experiments in support of the second part of the foregoing law:—When carbonic anhydride is driven over ignited charcoal, it is wholly converted into carbonic oxide; but when steam is transmitted over ignited charcoal, a mixture of hydrogen, carbonic oxide, and carbonic anhydride is produced, in the proportion of 4 volumes of hydrogen, 2 of carbonic oxide, and 1 volume of carbonic anhydride. Again, when a mixture of cyanogen with atmospheric air and oxygen was detonated in the eudiometer in the proportion of 6·2 of cyanogen to 10 of oxygen,\* the cyanogen yielded 3 volumes of nitrogen, 2 of carbonic oxide, and 4 of carbonic anhydride: and when a mixture of 4·07 of carbonic anhydride, 33·25 of hydrogen, and 10 of oxygen was detonated, a portion of the carbonic anhydride yielded oxygen to the hydrogen, and was reduced to the state of carbonic oxide; 3 volumes of carbonic oxide being formed, whilst exactly 2 volumes of carbonic anhydride remained unacted upon, although a large excess of hydrogen was present.

Debus arrived at substantially the same results with precipitates as those indicated by Bunsen for gaseous mixtures:—he precipitated a mixture of lime and baryta water, by small proportions of a solution of carbonic acid; and experiments upon a large excess of a dilute solution of the mixed calcic and baric chlorides to which a dilute solution of sodic carbonate was added, led to a similar result.

In the experiments of Bunsen, it must be recollected that the first products of the chemical combination are immediately removed from the sphere of action: carbonic anhydride, and carbonic oxide, and water will not mutually react upon each other; and in the experiments of Debus, the carbonates of the metals of the earths are insoluble—they are therefore at once withdrawn from further action upon the mixture.

(1003a) Messrs. Harcourt and Esson have attacked this problem in a different way. (*Phil. Trans.* 1865, 193; 1866, 117):—

Every chemical reaction is governed by certain general laws relating to the *quantity* of the substances which enter into it,

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\* Cyanogen requires for the complete combustion of its carbon twice its volume of oxygen, so that 6·2 of cyanogen would have required 12·4 instead of 10 of oxygen; there is therefore more oxygen than would suffice for the conversion of the carbon into carbonic oxide.



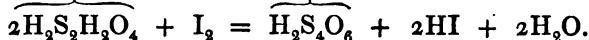
their *temperature*, their *physical state*, and the *time* during which they are in contact: yet the number of cases admitting of exact investigation is very limited. It must be possible to begin and end the reaction abruptly at a given moment so as to limit the time exactly; and it must be possible to determine accurately and easily one at least of the products of the reaction, so that the amount of the chemical change can be measured.

These conditions they attempted to fulfil by investigating the reaction of oxalic upon permanganic acid:—When a solution of potassic permanganate is added to a solution of oxalic mixed with diluted sulphuric acid, the red colour gradually disappears, owing to the reduction of the permanganic acid;  $K_2Mn_2O_8 + 3H_2SO_4 + 5H_2C_2O_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$ . The products are all soluble, the reaction occurs at moderate temperatures, and the time may be conveniently observed, and accelerated or retarded within wide limits. The action of oxalic acid upon the permanganate was found, however, not to be sufficiently simple; and after a laborious series of experiments they ascertained that another reaction, viz., that of hydric peroxide upon hydriodic acid, was better adapted to the purpose.

When solutions of potassic iodide and sodic peroxide are mixed in the presence of sulphuric acid a *gradual* separation of iodine takes place. Sodic and potassic sulphates are formed, and the liberated hydric peroxide and hydriodic acid undergo a change which may be thus represented:  $H_2O_2 + 2HI = 2H_2O + I_2$ . If sodic hyposulphite be added to the solution it *instantly* reconverts the iodine into hydriodic acid, but though the hyposulphite passes into a tetrathionate it appears in no way to affect the course of the reaction:

Hyposulphurous acid.

Tetrathionic acid.



Consequently, if the peroxide be in excess over the hyposulphite, the whole of the hyposulphite is gradually changed by the nascent iodine into tetrathionate; while the amount of hydriodic acid remains constant, and after the conversion of the hyposulphite is complete, free iodine again makes its appearance in the solution by the gradual action of the excess of hydric peroxide upon the hydriodic acid. The moment at which this liberation of iodine occurs can be most accurately observed by the previous addition of a little starch to the mixture.

In performing the experiment, measured quantities of the standard solutions of sulphuric acid, potassic iodide, and a filtered solution of starch were diluted with pure distilled water previously

boiled to free it from air, and allowed to cool in a vessel filled with carbonic anhydride, the glass cylinder in which the mixture was made being always filled up with the liquid to a given mark upon its side. A definite small measure of a solution of sodic hyposulphite was then added, and the reaction was commenced by the addition of 10 cub. centim. of a standard solution of sodic peroxide acidulated with sulphuric acid. The mass was kept continually agitated by the transmission of a stream of bubbles of carbonic anhydride, and the temperature was maintained uniform during the period of experiment. As soon as the blue colour manifested itself a note of the time was made, and a second measure of hyposulphite was added, by which the colour was instantly bleached, and the interval of time noted before the blue colour reappeared. A third measure of hyposulphite was then added, and so on in succession. The time that elapses between two successive appearances of the blue colour becomes continually greater in proportion as the amount of peroxide in the solution diminishes; finally, the last measure of hyposulphite requires for conversion into tetrathionate more oxygen than the peroxide can furnish, and the blue colour never returns.

By these experiments it was found that the amount of action varies directly with the variation in the amount of the active substance, the rate of action becoming slower as the quantity of peroxide diminishes. Harcourt and Esson state their general conclusion as follows:—"The amount of change varies directly (1) with the amount of iodide; and (2) with the amount of peroxide in a unit volume of the solution; (3) with the time during which the change proceeds; (4) with the total volume of the solution; and finally, with some function of each of the other conditions under which the change occurs."

(1004) *Adhesion*.—The influence of adhesion in aiding chemical action is often exerted by overcoming the opposite force of elasticity: this is exemplified by the manner in which water frequently favours the action of dry gases upon each other. For example, sulphurous anhydride and sulphuretted hydrogen may be mixed when dry without acting upon each other, but if water be present, the mutual decomposition of the two gases is the result. In like manner, when dry gaseous sulphurous anhydride and dry peroxide of nitrogen are mixed together, no combination takes place between them; the addition of a few drops of water, however, causes them immediately to condense and to form the white crystalline compound which has been spoken of when treating of the manufacture of sulphuric acid (412, and *note*

p. 178). If the elasticity of these gases be overcome by other means—if, for instance, they be liquefied by exposing them to a low temperature—combination occurs without the intervention of moisture.

Water, by overcoming the self-repulsion of the gases, favours their chemical action upon solid bodies. Hydrochloric acid, and ammonia, in their gaseous form, generally exert comparatively little influence upon the metals or upon their salts, although when in solution their action upon them is rapid and powerful.

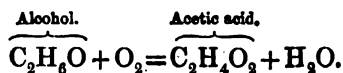
*Surface Actions.*—The adhesion of gases to solids produces many curious phenomena:—for example, let a piece of charcoal be thoroughly saturated with hydrogen by attaching it to the negative wire of the voltaic battery, and employing it as the platinode in the decomposition of acidulated water; this charcoal, if now detached from the battery and thrown into a solution of cupric sulphate, or of argentic nitrate, will effect the decomposition of these salts, and copper or silver will be thrown down upon the charcoal in the reduced state: the charcoal and condensed hydrogen appearing to act the part of a voltaic circuit, in which the hydrogen supplies the place of the electro-positive or oxidizable metal, and the charcoal that of the electro-negative metal or conducting plate. If a plate of platinum, rendered chemically clean,\* be introduced into a mixture of pure oxygen and hydrogen, in the proportions to form water, the gases become condensed upon the surface of the plate, and being brought within the sphere of each other's attraction, begin to unite; at first slowly, but during the act of combination heat is extricated, and the action proceeds more quickly, until at last the plate becomes red hot, and an explosion of the gas ensues (Faraday, *Phil. Trans.*, 1834, 55). By employing the metal in a disintegrated or spongy form, the surface exposed is greater, and the action much more rapid: the metal conducts away but little of the heat which is generated, and soon becomes red hot; whilst in the condition of platinum black (968) this activity attains its maximum. On throwing a little of this black powder into a mixture of oxygen and hydrogen it immediately becomes incandescent, and the gases combine with a loud report. Platinum

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\* This may be effected by holding the plate over the flame of a spirit-lamp and rubbing it, when hot, with a stick of caustic potash; the potash is to be maintained in a fused state upon its surface for a second or two; the alkali is then to be washed off completely in distilled water, and the plate is to be immersed for a minute in hot oil of vitriol; after which it is to be freed from adhering acid by immersion for a quarter of an hour in a large bulk of distilled water.

may be obtained in a convenient state of fine subdivision for experiments of this nature, by moistening asbestos with a solution of platinic chloride and exposing it to a red heat; the chlorine is expelled, and a film of minutely divided platinum is left upon the surface of each fibre of asbestos.

From its inalterability by ordinary chemical agents, platinum in this finely divided form has been used to effect various combinations which cannot otherwise readily be procured between vaporized and gaseous bodies:—For instance, if ammonia be mixed with atmospheric air, and transmitted over spongy platinum gently heated, its nitrogen becomes converted into nitric acid, and its hydrogen into water;  $\text{H}_3\text{N} + 2\text{O}_2 = \text{HNO}_3 + \text{H}_2\text{O}$ : but this transformation cannot be effected by heat, unless some substance analogous to spongy platinum be used, since nitric acid is decomposed at a temperature which, under ordinary circumstances, is required to effect the combustion of ammonia. On the other hand, ammonia may be formed from the oxides of nitrogen, by mixing them with hydrogen and transmitting the gases over platinum sponge gently heated;  $2\text{NO} + 5\text{H}_2 = 2\text{H}_3\text{N} + 2\text{H}_2\text{O}$ . Ammonic nitrate, when heated with platinum black, yields nitric acid, nitrogen, and water, instead of nitrous oxide; for instance,  $5\text{H}_4\text{NNO}_3 = 2\text{HNO}_3 + 4\text{N}_2 + 9\text{H}_2\text{O}$ . A variety of other interesting changes may be effected. According to Döbereiner (who first pointed out the remarkable power which finely divided platinum possesses of effecting combinations of this kind), a mixture of cyanogen and hydrogen when in contact with spongy platinum is partially converted by the aid of a gentle heat into ammonic cyanide. In a mixture of nitric oxide and olefiant gas, ammonic carbonate is produced; and in a mixture of the vapour of alcohol and nitric oxide,—ammonic cyanide and carbonate, olefiant gas, water, and a deposit of carbon are formed. In like manner, sulphurous anhydride may be converted rapidly into sulphuric acid, if it be driven, in a moist state, mingled with air, through tubes containing spongy platinum: this method was even proposed as a manufacturing process for obtaining oil of vitriol, but it was abandoned in consequence of a gradual alteration in the platinum, by which it is deprived of this power of effecting combination. Platinum black produces with the vapours of alcohol in contact with atmospheric air, a series of compounds which are finally converted into acetic acid and water:—



For the success of these experiments, it is necessary that the surface of the platinum be chemically clean, otherwise the combination of the gases does not take place. Faraday considered that these actions are owing to the adhesion of the gases to the surface of the metal, by which the particles of one gas are brought into chemical contact with those of the other. He observed that the admixture of small quantities of carbonic oxide, or of the vapour of carbonic disulphide, or of olefiant gas,\* prevents the platinum from effecting the combination of the oxygen and hydrogen, but does not deprive the metal of its activity, as he ascertained by afterwards plunging it into a mixture of pure oxygen and hydrogen. On the other hand, the addition of sulphuretted or of phosphuretted hydrogen to an explosive mixture of oxygen and hydrogen, not only prevents the combination from being produced by the platinum, but it effects such an alteration of the surface of this metal that when it is plunged into a fresh portion of mixed oxygen and hydrogen, no combination of the gases occurs. Hydrochloric acid also rapidly destroys the peculiar properties of finely divided platinum; according to Döbereiner, the preventive action of this gas depends upon the decomposition of the hydrochloric acid by the oxygen condensed upon the platinum: water is formed, whilst chlorine is liberated, and this chlorine, by converting the platinum superficially into chloride, destroys its power; its activity, however, can be restored by treating it with boiling oil of vitriol. Hydrochloric acid is in this case expelled, and a small quantity of platinous oxide is dissolved; the metal is then to be well washed in distilled water.

(1005) Other finely divided substances besides platinum possess this property of favouring the combination of oxygen and hydrogen in an inferior degree; even pounded glass, porcelain, charcoal, pumice, and rock crystal, if warmed to  $608^{\circ}$  ( $320^{\circ}$  C.), produce this effect. Finely divided palladium, rhodium, and iridium also determine the combination of oxygen and hydrogen with explosion at ordinary temperatures. Gold and silver effect the combination of hydrogen with oxygen quietly, at temperatures far below the boiling-point of mercury (Dulong and Thénard). Metals which have a strong chemical attraction for oxygen cannot

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\* Graham finds that in the case of carbonic oxide a gradual oxidation of the carbonic oxide takes place, but that this action is much slower than the oxidation of the hydrogen: the oxidizing influence is wholly concentrated on the carbonic oxide, and until this gas is entirely oxidated the hydrogen remains unaltered in the mixture.

be used, because they immediately become oxidized upon their surface.

(1006) *Catalysis*.—The remarkable actions produced by the agency of finely divided platinum have in the foregoing paragraphs been attributed to the force of adhesion, which is supposed to bring the different gaseous bodies within the sphere of mutual action; but they were viewed by Berzelius as arising from a new force, which he termed *catalysis*, in virtue of which, he says, "Certain bodies exert, by their contact with others, such an influence upon these bodies, that chemical action is excited; compounds are destroyed, or new ones are formed, although the substance by which these actions are induced does not take the slightest part in these changes." This catalytic force, however, is probably purely imaginary; most of the phenomena which have hitherto been referred to its agency being occasioned by several different causes, which often admit of being distinguished from each other, and which may, as in the case of the action of platinum, be explained by the active operation of other known forces.

One class of these phenomena is that included under the term *fermentation*. Fermentations are peculiar to the products of organic chemistry; such for instance, as the change of solution of sugar into alcohol and carbonic anhydride, under the influence of *yeast*: the change of starch into sugar in the operation of mashing wort, or in the germination of seeds, owing to the presence of a peculiar albuminous substance termed *diastase*: and the gradual conversion of amygdalin, the bitter principle in the bitter almond, into hydrocyanic acid, oil of bitter almonds, sugar, and formic acid, when it is dissolved in water, and mixed with *synaptase*, or the albuminous substance contained in the pulp of the seed. In all these cases, however, although the constituents of the yeast, the diastase, or the synaptase, do not enter into the formation of the new products, yet these bodies disappear during the change, and during the whole time are undergoing a series of specific alterations, which stand in intimate but as yet unexplained relation to the metamorphosis of the sugar, the starch, or the amygdalin. One of the most remarkable features of these decompositions is the small proportion of the ferment, or *catalytic body* as Berzelius termed it, which is required to produce the change: for instance, 1 part of yeast, calculated in its dry state, is sufficient to convert 60 parts of sugar into alcohol and carbonic anhydride; and a still smaller quantity is required in the case of diastase, 1 part of which is able, according to Payen, to effect the

transformation of more than 1000 times its weight of starch into sugar. The consideration of these remarkable metamorphoses must however be deferred until the organic bodies themselves have been described.

Liebig's theory of catalysis is, "that a body in the act of combination or decomposition enables another body with which it is in contact to enter into the same state. It is evident," says he, "that the active state of the atoms of one body has an influence upon the atoms of a body in contact with it, and if these atoms be capable of the same change as the former, they likewise undergo that change, and combinations and decompositions are the consequence. \* \* \* This influence exerted by one compound upon the other, is exactly similar to that which a body in the act of combustion exercises upon a combustible body in its vicinity; with this difference only, that the causes which determine the participation and duration of these conditions are different."

These explanations have been found insufficient to account for the phenomena of fermentation, as the bodies which are undergoing fermentation do not "enter into the *same* state" as the particles of the ferment; though they apply admirably to many of the illustrations cited by Liebig in support of his theory. Amongst these illustrations is an experiment by De Saussure, who observed that moist woody fibre, if placed in contact with oxygen, gradually converts the oxygen into carbonic anhydride. On adding a certain quantity of hydrogen to a measured bulk of oxygen, which was undergoing this change, he observed a diminution in the volume of the two gases immediately after making the mixture; a portion of oxygen had thus been caused to enter into combination with the hydrogen, and a true gradual combustion of the hydrogen had been effected, analogous to that produced by platinum, owing to its contact with vegetable matter which was itself undergoing slow oxidation.

Again, it has been observed in the case of certain alloys, that the compound is entirely soluble in an acid which may be unable to attack one of the components of the alloy when in a separate form. Platinum, for instance, is not soluble in nitric acid, but if it be alloyed with 10 or 12 parts of silver, the acid dissolves it readily. In like manner, copper is insoluble in diluted sulphuric acid; but an alloy of zinc, nickel, and copper is readily dissolved by this liquid.

(1007) *Effects of Motion on Chemical Attraction.*—In many cases motion favours the manifestation of cohesion in a remarkable

manner: for example, water may be cooled below its freezing-point, and may retain its liquid form if it be kept perfectly motionless, but on the slightest agitation it assumes the form of ice. Again, if a solution of argentic nitrate be simply mixed with hydrochloric acid, it will long remain milky; but if the nitrate be in excess, and the mixture be briskly shaken for about a minute, the whole of the argentic chloride will collect into dense flocculi, which subside rapidly and leave the liquid clear. In a somewhat similar manner motion favours the development of chemical action:—when, for example, a mixture of tartaric acid and potassic nitrate is made, no sign of precipitation will appear for many minutes, if the mixture after simple agitation be left at rest: but if it be stirred briskly with a glass rod, an abundant deposition of crystals will speedily be produced. A similar effect is often observed with other crystalline precipitates: for instance, the potassio-platinic, or ammonio-platinic chloride, frequently does not appear in dilute solutions until the mixture has been briskly stirred. If the glass rod which is used in stirring the mixture be drawn against the side of the vessel containing the liquid, the track of the rod will be rendered evident by the formation of crystals, which are symmetrically deposited on each side of this line. This effect is particularly manifested when a solution of hydro-disodic phosphate is added to dilute neutral magnesian solutions containing ammoniacal salts; the crystalline ammonio-magnesian phosphate takes many hours for its complete deposition, unless the liquid be briskly stirred.

Sometimes when the chemical attractions which hold a compound together are feeble, or where the components have a strong tendency to assume the gaseous form, a blow will be sufficient to disturb the equilibrium, and an explosion will follow. In this way the compound known as chloride of nitrogen, which is united by feeble ties, and is composed of bodies which naturally exist in the gaseous state, is sometimes decomposed by the mere fall of a drop of the liquid to the bottom of a jar of the solution in which it is being formed. The ordinary percussion-cap is another instance of the same kind, where the nitrogen in the fulminate suddenly resumes its gaseous state on the application of a blow. In the latter case, and in that of the common lucifer match, it might be supposed that the heat evolved by the sudden compression attending the blow or the friction, is the cause of these detonations; but this explanation certainly cannot apply to the so-called iodide of nitrogen, which, if dry, explodes when touched



even with a feather. Fulminating silver is also decomposed with explosion by causes equally slight.

(1008) *Concurring Attractions*.—Another class of these so-called catalytic phenomena is exemplified in the effect of the admixture of cupric oxide, or manganic dioxide, in aiding the decomposition of potassic chlorate. This chlorate fuses at about  $653^{\circ}$  ( $345^{\circ}$  C.), and when heated to about  $698^{\circ}$  ( $370^{\circ}$  C.) it is decomposed with effervescence and a rapid evolution of oxygen: when mixed with about a fourth of its weight of cupric oxide, or of manganic dioxide, the salt begins to be decomposed at a temperature of between  $230^{\circ}$  and  $260^{\circ}$  C. (much below its fusing-point); the gas which is given off in this case, however, is always accompanied by a small quantity of chlorine. Other oxides produce a similar effect, but the temperature required varies with each oxide; thus, I find when the chlorate is mixed with ferric oxide it requires a temperature of about  $500^{\circ}$  ( $260^{\circ}$  C.); with plumbic oxide a somewhat higher temperature is needed; whilst magnesia and zincic oxide do not aid the decomposition of the salt at all.

This remarkable decomposition appears to admit of an explanation, suggested by Mercer, in elucidation of other somewhat analogous actions. He supposes, although the catalytic body is not found to have experienced any perceptible alteration after the decomposition is complete, that it acts by exerting a feeble chemical attraction upon one of the constituents of the compound. In the case of manganic-dioxide and potassic chlorate, the manganic dioxide is a substance which has an attraction for an additional quantity of oxygen, as is evinced by the possibility of forming manganic and permanganic acids from it by further oxidation. This tendency, although it does not rise high enough in the experiment before us to produce either acid, may yet exert sufficient attraction upon the oxygen to facilitate its escape. Indeed it is not impossible that traces of potassic manganate may be actually formed, and then decomposed; in which case the formation of the small quantity of potash, and the liberation of the chlorine, which always accompanies the oxygen, would be accounted for. A somewhat similar explanation may be applied in the case of the cupric oxide; an unstable sesquioxide of copper appears to exist; cupric oxide therefore has a feeble attraction for oxygen, and though that attraction is not adequate to retain the oxygen when separated from the potassic chlorate, it may yet aid in effecting its liberation: ferric oxide is also susceptible in the ferric acid of a higher but unstable stage of oxidation, and the same holds good of plumbic oxide; hence these compounds facilitate the decom-

position of the chlorate. There is no proof of the existence of a higher oxide either of magnesium, or of zinc, and accordingly we find that scarcely any effect is produced on heating these oxides with the chlorate. I have found also that powdered glass and pure silica are equally inert, probably from the same cause.

Mercer observed that starch, which is ordinarily converted by nitric acid into oxalic acid, is entirely transformed into carbonic anhydride if a salt of manganese be present;  $2\text{CO}_2$  being formed, instead of  $\text{H}_2\text{C}_2\text{O}_4$ . Oxalic acid, also, may be in this manner converted rapidly into carbonic anhydride. If 30 grms. of oxalic acid be dissolved in 300 cub. centim. of water, at  $180^\circ$  ( $82^\circ\cdot 2$  C.), and 30 c. c. of colourless nitric acid, sp. gr. 1.30 be added, no decomposition of the oxalic acid occurs: but it immediately commences on adding a small quantity of a solution of manganous nitrate, or any other manganous salt. The manganous oxide, from its tendency to pass into the state of dioxide, tends to deprive the free nitric acid of oxygen, and aids the oxalic acid to decompose this acid; and the oxalic acid having a stronger attraction for oxygen than manganous oxide has, immediately appropriates the oxygen; the united attractions of both being able to accomplish a decomposition which could not have been effected by either separately. An analogous instance of the effect produced by concurring attractions of a more energetic kind is seen in the power possessed by chlorine to decompose silica or alumina when these oxides are mixed with charcoal and ignited (475, 664), though neither chlorine nor charcoal is able separately to produce this effect upon them.

A similar result is obtained when a quantity of hydrated cupric oxide, or of manganic dioxide, is thrown into a mixture of bleaching powder and water; on warming the mixture, oxygen is evolved abundantly, and calcic chloride is formed; the cupric or manganic oxide, by its attraction for oxygen, aids the elastic force developed by heat in detaching the oxygen from the chloride of lime, and the oxygen, by its elasticity, escapes in the gaseous form without combining with the metallic oxide.

Gaseous ammonia may be passed through heated porcelain tubes at a very high temperature, and it will experience only a partial decomposition; but if the tube be filled with finely divided metallic copper or iron, the decomposition takes place with facility at a lower temperature. It appears that in this case the metals act by their attraction for nitrogen, which is feeble, and that a nitride of copper or of iron is formed and subsequently decomposed. If iron wire be employed instead of finely divided iron,

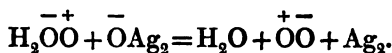
it is found to have become superficially altered and brittle (760). Platinum favours the decomposition of ammonia but slightly, and glass scarcely in any appreciable degree.

Alcohol when exposed to the air, evaporates without undergoing any chemical change, but if a quantity of caustic potash be dissolved in the alcohol, the alkali appears to enhance its attraction for oxygen; in consequence of which acetic and formic acids are produced, and form salts with the potash.

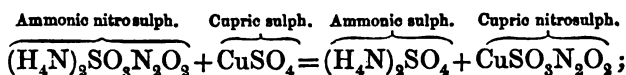
The decomposition of hydric peroxide ( $H_2O_2$ ; 485), by contact with many bodies which appear to undergo no chemical alteration during the action, may probably be referred to the same cause. When, for example, finely divided metallic gold, silver, or platinum, or manganic dioxide, is placed in the liquid peroxide, the latter is decomposed, the oxygen being attracted by the metal, which, however, has not sufficient power to retain it in combination. A singular circumstance, however, has been observed when auric or argentic oxide is substituted for the metal itself; decomposition of the peroxide is produced by the metallic oxide, but the auric or argentic oxide at the same time parts with its oxygen, and is reduced to the metallic state. A similar reaction happens if an acid solution of potassic dichromate be mixed with the hydric peroxide, the chromic acid losing half its oxygen simultaneously with the hydric peroxide.

Brodie (*Phil. Trans.* 1850, 759, and 1862, 837) has published the results of a series of experiments, showing that in such decompositions there is a numerical relation between the quantity of the peroxide which is decomposed, and of the metallic oxide which is reduced. These experiments were not confined to hydric peroxide, but were extended to baric and sodic peroxides, which are much more manageable than hydric peroxide. It was found that when the peroxide is mixed with water, and placed in contact with argentic oxide or chloride, that both the compound of barium and that of silver is decomposed; baryta, or baric chloride, being formed, whilst metallic silver and oxygen gas are liberated. When a dilute solution of potassic permanganate is mixed with an acid solution of hydric peroxide, both compounds are decomposed, the permanganate losing an atom of oxygen for each atom of oxygen liberated from the peroxide. A similar decomposition occurs if baric hypochlorite be substituted for potassic permanganate. Brodie connects these experiments with a hypothesis since generally adopted, by which he accounts for the simultaneous liberation of oxygen from the hydric or baric peroxide, and from the argentic oxide or other oxide which under-

goes decomposition, and which he applies to chemical decompositions generally: he supposes that the *particles of the same element* may, in certain circumstances, have an attraction for each other:—that, for example, one atom of the oxygen of the baric peroxide may be positive in its relation to the oxygen of the argentic oxide, which he supposes may be negative. In such a case the two particles of oxygen would mutually attract each other, and decomposition of both the oxides would be the result.



Other substances, besides the hydric and the alkaline peroxides, exhibit a similar susceptibility to decomposition by contact with certain bodies. Hydric persulphide, for example, is immediately decomposed by contact with oxides of manganese and silver, and, like hydric peroxide, it is rendered more stable by the addition of acids, while its decomposition is facilitated by contact with alkalis (429). The nitrosulphates (425) discovered by Pelouze afford another instance of decomposition effected by a body which undergoes no *apparent* change; but this decomposition is particularly instructive, as it is almost certain that the body which excites the decomposition does suffer a *real* chemical change. For example, the addition of a solution of cupric sulphate to a solution of ammoniac nitrosulphate causes an immediate effervescence, owing to the escape of nitrous oxide. This decomposition appears to be produced thus:—on the addition of cupric sulphate, the nitrosulphate partially exchanges basyls with it; now so long as the nitrosulphuric radicle is in combination with an alkali-metal, the compound has a certain stability, since the alkali-metals appear by their basic energy to preserve the elements *in equilibrio*; but as soon as a salt with a weaker basyl is added, such as cupric sulphate, a portion of cupric nitrosulphate is formed; but the copper being no longer able to maintain this balance, the elements of the compounds arrange themselves in a new order: for instance—



and the cupric nitrosulphate immediately breaks up into nitrous oxide, and cupric sulphate;  $\text{CuSO}_3\text{N}_2\text{O}_2$  becoming  $\text{CuSO}_4 + \text{N}_2\text{O}$ . Consequently cupric sulphate is found in the liquid at the close of the reaction apparently unaltered.

## § II. INFLUENCE OF HEAT UPON CHEMICAL ATTRACTION.

(1009) THE forces which have as yet been considered do not manifest any specific effect in altering the amount of chemical attraction between any two bodies; but it is quite otherwise in the case of heat, which exerts a direct influence upon the degree of attraction. Elevation of temperature generally acts at once in augmenting the tendency to combination between the bodies which are submitted to its influence:—for example, sulphur or charcoal may be preserved at ordinary temperatures, in air or in oxygen, without change for an indefinite period; but if sulphur be heated to  $500^{\circ}$  ( $260^{\circ}$  C.), and charcoal to a point a little below a red heat, oxidation commences, and proceeds with increasing vigour, and the phenomena of combustion occur. But although a rise of temperature exalts the action of chemical attraction, this tendency to combination is, at the same time, more or less counteracted, and is sometimes completely overcome, by the tendency to mutual repulsion which heat imparts to the molecules of all substances, both simple and compound. It not unfrequently happens that a moderate elevation of temperature produces combination, whilst a higher temperature destroys the compound so formed. A good instance of this kind occurs in the action of oxygen upon mercury; at ordinary temperatures this metal shows no disposition to combine with oxygen, for it evaporates in air and becomes condensed again in the metallic form; but at a temperature approaching  $698^{\circ}$  ( $370^{\circ}$  C.), or a little above the boiling-point of the metal, it combines gradually with oxygen and becomes converted into the red oxide; whilst at a heat short of redness it is decomposed into gaseous oxygen and vapour of mercury. Again—baryta at a red heat absorbs a second atom of oxygen, forming baric peroxide, but the second atom of oxygen is expelled by a full white heat, and the compound is reconverted into baryta. A mixture of oxygen and hydrogen may be preserved unchanged at ordinary temperatures, but the introduction of a glass rod heated to bare redness so completely alters their mutual attraction, that sudden combination attended with explosion is the result. This appears to be as pure a case of augmentation of chemical attraction as can be met with, since both the components are thoroughly mixed, and as both are in the gaseous state, heat cannot in this case act by diminishing cohesion, and so bringing their particles into more intimate contact. Grove, however, has shown that in the case of this same compound of oxygen and hydrogen a sudden

inversion of chemical attraction takes place, for at an intense white heat water is separable into its constituent gases: by the voltaic ignition of a platinum wire under water, or by the intense heat of a ball of melted platinum raised to whiteness by an alcohol flame animated by a current of oxygen, and then plunged under water, the two gases may be separated from each other and collected in the gaseous state (*Phil. Trans.* 1847).

(1010) *Dissociation*.—When a rapid current of carbonic anhydride, mixed with steam, is transmitted through a porcelain tube of 2 inches or  $2\frac{1}{2}$  inches (from 5 to 7 cm.) in diameter, which has been filled with clean and previously ignited fragments of porcelain, and the tube is heated intensely in a blast-furnace or forge, it is found that the gas which is left after absorbing the excess of carbonic anhydride by means of caustic potash consists of an explosive mixture of oxygen, hydrogen, carbonic oxide, and nitrogen: in two experiments from 25 to 30 cubic centimetres of the mixed gases (from  $1\frac{1}{2}$  to 2 cubic inches) were obtained, consisting of—

					I.	II.
Oxygen	...	...	...	...	46.1	46.8
Hydrogen	...	...	...	...	35.4	31.9
Carbonic oxide	...	...	...	...	12.0	10.7
Nitrogen	...	...	...	...	6.5	10.6

Water has here been decomposed into its constituents, part of the liberated hydrogen has exerted a reducing action on the carbonic anhydride, and part of the hydrogen has escaped reoxidation by its copious dilution with other gases. The presence of nitrogen is due to the entrance of atmospheric air, for however carefully the gases are prepared, it is nearly impossible in an experiment of this kind, which lasts for a couple of hours, to exclude the air perfectly.

A still larger proportion of the explosive mixture is obtained by placing a tube of porous earthenware in the axis of a shorter but wider tube of glazed porcelain, fitting them air-tight with corks, and transmitting a current of any gas at pleasure through the inner tube, and through the interval between the two tubes. By a suitable arrangement of glass tubes the gases may be collected from either tube separately, and the effects of heating the tubes can be observed upon the issuing gases: for example, if the tube be heated to from  $1100^{\circ}$  to  $1700^{\circ}$  C. (or from about  $2000^{\circ}$  to  $3000^{\circ}$  F.) and a current of steam be transmitted through the inner tube, whilst carbonic anhydride is passed through the outer one, an explosive mixture, similar to that already described, is obtained, but in larger quantity. The hydrogen, at the moment

that it is liberated by the effect of heat from its combination with oxygen, at once becomes diffused through the porous tube into the outer one, and there reduces the carbonic anhydride, whilst the less diffusible oxygen passes on.

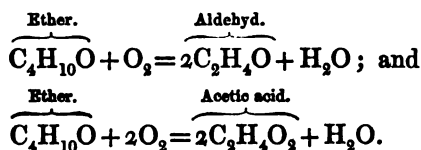
In like manner, if a brisk current of pure carbonic anhydride be transmitted through a porcelain tube filled with fragments of porcelain, and the temperature be raised to  $2372^{\circ}$  ( $1300^{\circ}$  C.),—after absorbing the carbonic anhydride, a mixture of two volumes of carbonic oxide and one of oxygen, with a little nitrogen, was obtained. To this partial decomposition at elevated temperatures Deville gives the name of *dissociation*. During the occurrence of this phenomenon an absorption of latent heat takes place, analogous in some measure with that which occurs in the evaporation of liquids at temperatures below their boiling point. The dissociation of compound gases has been carried still further. Carbonic oxide may be resolved into carbon and carbonic anhydride by the following arrangement:—A porcelain tube is placed across a furnace, the temperature of which can be raised very high. In the axis of this tube is supported a thin brass tube of about  $\frac{1}{4}$  inch ( $8^{\text{mm}}$ ) in diameter, through which a current of water is kept flowing. Through the outer tube a current of pure carbonic oxide is maintained, transmitting from 4 to 6 litres, or from 250 to 350 cubic inches of the gas per hour. The porcelain tube is gradually raised to bright redness, and on causing the escaping gas to pass through baryta water, a precipitate of baric carbonate is gradually formed, and a layer of black carbon is deposited upon the under surface of the brass tube, where the current of ascending heated gas strikes against the cooled metal. A similar decomposition may be effected by transmitting a current of electric sparks through carbonic oxide over mercury, upon which a few drops of concentrated potash ley have been placed to absorb the carbonic anhydride as it is formed.

When instead of carbonic oxide, pure and dry sulphurous anhydride is transmitted through the porcelain tube, the gas becomes solved partially into sulphur and sulphuric anhydride. The metallic tube in this case was made of copper thickly plated with a voltaic deposit of silver. If this tube be amalgamated, and current of pure and dry hydrochloric acid be transmitted through the ignited porcelain tube, heated to at least  $2732^{\circ}$  ( $1500^{\circ}$  C.), whilst the temperature of the metallic tube is reduced below  $50^{\circ}$ , a deposit of chloride of mercury and chloride of silver is formed in a few hours, and a small quantity of hydrogen may be collected. Traces of decomposition of hydrochloric acid may be effected by

the continuous discharge of electric sparks for 3 or 4 days through the dry gas; and with sulphurous anhydride the decomposition is easy. Carbonic anhydride is also readily decomposed by the electric spark if a little piece of phosphorus is passed up into the tube to absorb the liberated oxygen.

Sometimes the decomposition effected by elevation of temperature is only partial; a new and more stable compound being formed, which at a still higher temperature is in its turn decomposed: for example, olefiant gas at a full red heat loses half its carbon, and is converted into light carburetted hydrogen; and this gas, if subjected to a white heat, deposits the remainder of its carbon, while pure hydrogen is liberated. Potassic chlorate at a moderate heat is decomposed into perchlorate, and probably into chlorite: the latter salt, however, is immediately resolved into oxygen and potassic chloride; but at a higher temperature the perchlorate in its turn parts with its oxygen, and the more stable potassic chloride is the final result. Numerous other instances of this kind will be presented to the reader when the products of organic chemistry are examined.

A further illustration of this point is afforded by the different products which are furnished by the combustion of the same body at different temperatures. When a jet of cyanogen is burned with a free supply of air, the only products of the combustion are carbonic anhydride and nitrogen; but if a coil of red-hot platinum wire be suspended in a mixture of equal volumes of cyanogen and oxygen, the nitrogen undergoes oxidation as well as the carbon, nitric oxide being formed, as is evidenced by the appearance of ruddy fumes, owing to the combination of the nitric oxide with free oxygen. In a similar manner, ether, when burnt freely in air, produces carbonic anhydride and water,  $C_4H_{10}O + 6O_2$  becoming  $4CO_2 + 5H_2O$ ; but if a glowing coil of platinum wire be suspended in a mixture of the vapour of ether and atmospheric air, several new products are formed, among which are aldehyd and acetic acid:—



(1011) *Suspension of Chemical Action by Depression of Temperature.*—As chemical attraction is increased, on the one hand, by elevation of temperature, so, on the other hand, it is diminished by reduction of temperature. Schrötter has shown (*Chemie*, vol. i.



p. 129) that, by a sufficient degree of cold, chemical combination may be prevented even between bodies which at the ordinary temperature of the air unite with each other with great energy. Chlorine, for example, combines with phosphorus, or with finely-divided metallic antimony or arsenicum, with such violence that these bodies take fire spontaneously in an atmosphere of the gas; but if the chlorine be cooled down to  $-105^{\circ}$  ( $-76^{\circ}.1$  C.), by means of a bath of solid carbonic anhydride and ether, it remains liquid at the ordinary pressure of the air, and it is then quite indifferent to the phosphorus, the arsenicum, or the antimony, provided these substances be cooled to the same temperature before they are added to the liquid chlorine. When the tube in which the mixture is contained is withdrawn from the cold bath, the evaporation of the chlorine occurs with sufficient rapidity to preserve the temperature below the point of combination; but if the free escape of the chlorine be prevented, the temperature rises, and combination occurs with explosive violence. The mutual action of chlorochromic acid and alcohol, of chlorine and ammonia, of iodine or of bromine and phosphorus, and various other actions of a similar nature, may be prevented in the same way.

From these experiments, and from those detailed in the foregoing paragraph, it appears to be most probable that when two bodies have a chemical attraction for each other, there is a certain range of temperature within which they will enter into combination, but if the temperature be raised or depressed beyond a certain limit, their mutual attraction is suspended; and at high temperatures the compound already formed may be destroyed. The temperature most favourable for combination varies with each pair of bodies, and it seems to be probable that there is for each a certain temperature at which the maximum of attraction exists, and above or below which it decreases.

The influence of light in modifying chemical action is extremely important, but its principal effects have already been considered (Part I. pp. 214 *et seq.*).

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## CHAPTER XXI.

### ON THE DETERMINATION OF THE COMBINING NUMBERS, AND THE ATOMIC WEIGHTS OF THE ELEMENTARY BODIES.

(1012) *Aid derived from Analysis in Fixing the Atomic Weight of a Body.*—The determination of the atomic weight of

an element involves the performance of analytical operations of great delicacy, and it often presents many very difficult questions for solution. The first object of the chemist is to select some compound of the elementary body under examination, the composition of which is tolerably simple, and which can readily be procured in a state of purity; and in this compound he determines the proportions of each of its components with the utmost attainable precision. It is of great importance that the operations by which these results are obtained should be as few in number and as simple and manageable as possible. It is not, however, sufficient that three or four different experiments conducted in the same manner should give uniform results: the mode of analysis adopted should, if possible, be varied so as to avoid any unperceived source of error which depends upon the process employed. It is also desirable to vary the compound upon which the analysis is made. For example, the atomic weight of a metal may in some instances be ascertained by fixing the proportion of oxygen which a given weight of the metal absorbs during its conversion into the state of oxide: in other cases the proportion of oxygen and of metal can be determined very exactly by ascertaining the loss of weight which the oxide experiences when a known weight of the pure oxide is heated in a current of hydrogen. It is, however, advisable to check these results, not only by trials upon different quantities of the metal or of the oxide prepared at different times, but also (in order to guard against the occurrence of any unperceived impurity in the substance under experiment) to ascertain if the analysis of the chloride, the sulphide, or some other compound of the metal, gives a similar numerical value for its combining proportion. These results must be reduced by calculation to their weight *in vacuo* (24).\*

(1013) *Aid derived from Isomorphism, Specific Heat, and Combining Volume of Vapour.*—The determination of the numbers which are assumed to represent the relative atomic weights of the elements, however, does not rest simply upon the knowledge of the proportion in which each element enters into combination with a given amount of oxygen or of any other simple body. When a substance forms but a single combination with oxygen, the simplest hypothesis respecting its composition is that the compound so formed is produced by the union of single atoms of each of its components.

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\* Some idea of the extraordinary care required in researches of this description may be formed by the perusal of the admirable memoirs of Stas, in the Transactions of the Brussels Academy for 1860 and 1865.

Magnesium and zinc, for example, each forms but a single oxide, which is assumed to be a protoxide,—or oxide each compound atom of which contains 1 atom of the metal to 1 atom of oxygen. The nitrates formed from such oxides, if represented as consisting of the anhydride and the oxide,  $M''O, N_2O_5$ , will contain a quantity of the anhydride ( $N_2O_5$ ), in which the proportion of oxygen is five times that of the base. But it not unfrequently happens that the same metal forms two oxides, in one of which a given weight of oxygen combines with twice as large a proportion of the metal as in the other; for example, 16 parts of oxygen unite with either 63.5 of copper to form the black oxide, or with 127 of the metal to form the red oxide; and corresponding salts may be obtained by the reaction of each oxide with acids. In like manner, 16 parts of oxygen form with mercury two basic oxides, one containing 200, the other 400 parts of mercury. The question to be determined then is, which of these numbers is to be regarded as representing the atomic weight of the metal? In cases of this kind, the judgment requires aid from analogy, or from collateral circumstances, such as the isomorphism of the body with some other analogous compound of known composition; the circumstance that the specific heat of the body, when multiplied into its supposed atomic weight, yields the same product as that obtained by multiplying the specific heat of some other element into its admitted atomic number; or the formation of a volume of vapour from the supposed atomic weight which is equal in bulk to the volume of the atom of hydrogen.

Such assistance is afforded in the case of copper by the isomorphism of the compounds of the black oxide of this metal with corresponding compounds of zinc and magnesium. If the oxide of zinc be a protoxide, the black oxide of copper is also a protoxide, and the red oxide must be considered as a suboxide.

Another character of high importance is afforded by the specific heat of the metal. Assuming the oxide of zinc to be a protoxide, the atomic number of the metal is 65.0, and its specific heat is found to be 0.0955; the product of these two numbers is 6.207. The specific heat of copper is 0.0951, and assuming the black oxide to be the protoxide, the atomic weight of the metal is 63.5; the product of these two numbers is 6.039, or nearly the same as in the case of zinc; whereas, if the red oxide were assumed to be the protoxide, it would be double this number. If the numbers given upon pp. 24, 25, Part I., as the atomic weights of the elements, be multiplied by the specific heat of these bodies in the solid form (Part I. p. 313), the products so obtained will vary but

little from the number 6. Exceptions occur in the case of carbon, silicon, and boron, where allotropic modifications interfere. (See also Kopp, *Phil. Trans.* 1865).

In the determination of the atomic weights of volatile bodies, assistance may be derived from another character of great importance, viz., the density of its vapour. But the force of this argument will be more fully perceived after the various compounds of organic chemistry, of which so large a proportion are volatile, have been examined.

It is not safe, moreover, to assume in cases in which only one compound exists between an element and oxygen, that such compound is necessarily a protoxide; aluminum is not known to form more than a single oxide, yet chemists do not hesitate to consider this oxide as a sesquioxide, and in this judgment they are guided by analogy: for example, those bodies which are admitted to be protoxides are generally powerful bases, and neutralize the acids very completely. Now alumina does not present this character; its salts have a powerfully acid reaction and taste. But the arguments of most weight against the supposition that alumina is a protoxide are derived from the composition and properties of the oxides of iron. Iron forms two basic oxides: one contains but two-thirds of the proportion of oxygen which is present in the other. The oxide of iron with the smaller proportion of oxygen is a powerful base, and with acids forms salts which are isomorphous with those of magnesia and zincic oxide. It is consequently regarded as a protoxide, and the other oxide is looked upon as a sesquioxide; the basic properties of the latter are much more feeble, and the salts which it forms with acids have, like the salts of aluminum, a powerfully acid reaction. Ferric oxide, moreover, furnishes salts which are isomorphous with those of alumina. An iron alum may be obtained in octohedral crystals, in which the place of the aluminic sulphate is supplied by ferric sulphate: and native ferric oxide is found in forms of the rhombohedral system isomorphous with native alumina in corundum. Hence, if the red oxide of iron be a sesquioxide, alumina must be a sesquioxide also. Moreover, the specific heat of aluminum follows Dulong's law if alumina be a sesquioxide, but not if it be supposed to be a protoxide.

An excellent illustration of the value of isomorphism in these cases is also afforded by the oxides of chromium. Until the publication of Pélignot's researches on this metal, only two compounds of chromium with oxygen were known, viz., the green oxide, and chromic anhydride,—the anhydride containing twice as much

oxygen as the oxide. In these two compounds the proportion of oxygen combined with equal weights of chromium was as 1 : 2, or as  $1\frac{1}{2}$  : 3. But there was little difficulty in deciding that the green oxide must be regarded as a sesquioxide, for the green oxide of chromium was known to be isomorphous with the red oxide of iron, both in its uncombined form, and in the salts which it yields by action upon the same acids. Chromic anhydride would therefore contain three atoms of oxygen to 1 atom of the metal. But evidence still more conclusive of the accuracy of this view is afforded by the fact that the chromates are isomorphous with the manganates; now the manganates are known to contain 4 atoms of oxygen, for they are the salts of the acid of a metal which yields a basic oxide with a given weight of manganese containing one-fourth of the oxygen present in manganic acid,  $H_2MnO_4$ , and which moreover is isomorphous with the ferrous oxide. Finally, the discovery of another oxide of chromium, with a smaller proportion of oxygen than either of the compounds previously known, fully vindicated the correctness of the foregoing deductions; for the new oxide was found to contain one-third of the proportion of oxygen present in chromic anhydride. It also yields salts isomorphous with the corresponding salts obtained from the protoxide of iron, and the proportion of oxygen which it contains bears the same relation to that present in the green oxide of chromium that the oxygen in the protoxide of iron does to that in the red oxide of iron. Péligot's new oxide therefore was the missing protoxide of chromium.

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(1014) *Numerical Data from which the Equivalents and Atomic Weights of the Elements have been calculated.*

The combining proportions of the elementary substances were first investigated with precision by Berzelius, and the numbers obtained by him, with certain important corrections, are those at present in use. These researches of Berzelius, combined with those of subsequent chemists, particularly of Dumas (*Ann. de Chimie*, III. i. 5; viii. 189; and lv. 129); of Pelouze (*Comptes Rendus*, xx. 1047); of De Marignac (*Bibliothèque Univ. de Genève*, xlv.); of Erdmann and Marchand (*Journal für prakt. Chemie*, xxiii., xxvi., xxxi., and xxxiii.); and of Stas (*Trans. Brussels Academy*, 1860, 1865), have furnished the following data, from which the numbers given at pp. 24, 25, Part I., have been compiled:—

1. *Aluminum*.—Berzelius found that 100 parts of aluminic sesquisulphate ( $Al_2SO_4$ ) lost by intense ignition 70.066 of sulphuric

anhydride; hence assuming the atomic weight of  $\text{SO}_4$  as 96, that of aluminum (hydrogen being = 1) is 27.344. Dumas, by determining the amount of silver required to precipitate a given weight of aluminic chloride ( $\text{Al}_2\text{Cl}_6$ ), obtained numbers, from a mean of seven experiments, indicating that the atomic weight of aluminum is 27.488.

2.—*Antimony*.—The number 129.03, assigned by Berzelius to antimony, is admitted to have been too high. Schneider, by reducing the native sesquisulphide ( $\text{Sb}_2\text{S}_3$ ) to the metallic form, obtained on the average 71.469 per cent. of metal, which would yield as the combining number 120.3. The experiments of Rose on the trichloride ( $\text{SbCl}_3$ ) gave 120.69. Dexter, by oxidizing the metal with nitric acid, and converting the residue by ignition into  $\text{Sb}_2\text{O}_4$ , obtained 122.34 as a mean result; and Dumas by experiments upon the trichloride found the quantity of silver required to precipitate this chloride indicated 122.0, as the combining number of the metal, which we have adopted.

3. *Arsenicum*.—Pelouze decomposed a given weight of arsenious chloride ( $\text{AsCl}_3$ ) by means of water, and determined the quantity of argentic chloride which it produced: a mean of three experiments furnished 75 as the atomic weight of arsenicum, a result confirmed by four experiments of Dumas, which gave it as 74.95.

4. *Barium*.—Berzelius found that 100 parts of baric chloride ( $\text{BaCl}_2$ ), when dissolved in water, yielded 112.175 of baric sulphate ( $\text{BaSO}_4$ ), on the addition of sulphuric acid; and that 100 parts of the chloride when mixed with a solution of argentic nitrate yielded 138.07 of argentic chloride. Pelouze, by precipitation with silver, obtained results almost identical: the number calculated from the results of Berzelius for barium is 136.84; from those of Pelouze, 137.28. De Marignac, from a series of experiments of the same kind, checked by the determination of the barium as sulphate, obtained the number 137.16; and a mean of sixteen experiments conducted in a similar manner by Dumas leads to the number 137.02.

5. *Bismuth*.—100 parts of the metal converted into nitrate and decomposed by heat in a glass vessel, gave 111.275 of sesquioxide,  $\text{Bi}_2\text{O}_3$ , hence the atomic weight of bismuth is 212.86 (Lagerhjelm). Dumas, from a mean of seven experiments upon the quantity of silver required to precipitate the chlorine from a given weight of bismuth chloride ( $\text{BiCl}_3$ ) obtained 210.34 as the number for this metal. 210 is the number admitted.

6. *Boron*.—According to Berzelius, 100 parts of borax lost

47.1 of water, and yielded 16.31 of soda, leaving for boracic anhydride  $B_2O_3$  (by difference) 36.59; and Davy found, by the direct combustion of boron, that 100 parts of boracic anhydride contain 32 of boron and 68 of oxygen. This would make the number for boron 10.9. But the methods which were employed are admitted by Berzelius not to be such as to warrant entire confidence in the accuracy of this number; and Deville, from his experiments upon boric trichloride and tribromide, regards 11 as nearer the truth.

7. *Bromine*.—De Marignac found that 3.946 grammes of silver, when dissolved in nitric acid, required 4.353 grammes of potassic bromide (KBr) for its complete precipitation; and 15.00 of silver converted into nitrate gave 26.11 of argentic bromide: taking the atomic weight of silver at 107.97, a mean of the experiments gives the number for bromine as 79.97; and this result has been verified by Dumas by the decomposition of bromide of silver in a current of chlorine. It may without sensible error be taken as 80.

8. *Cadmium*.—Stromeyer found that 114.352 parts of cadmic oxide ( $CdO$ ) yielded 14.352 of oxygen; from which the atomic weight of this metal is 111.48. Dumas, as a mean of six experiments upon the quantity of silver required to precipitate the chlorine from a given weight of cadmic chloride ( $CdCl_2$ ), obtained results represented by the number 112.24; but his experiments were not quite so concordant as usual.

9. *Calcium*.—Dumas, by the ignition of 100 parts of Iceland spar ( $CaCO_3$ ) obtained 56 parts of lime, which would make the atomic weight of calcium exactly 40: and the mean of later experiments by the same chemist upon the quantity of silver required to precipitate a given weight of calcic chloride ( $CaCl_2$ ), leads to the number, 40.02. Erdmann and Marchand's results would make it 40.06; De Marignac's, by decomposition of a known weight of calcic chloride, 40.21; and those of Berzelius, by the conversion of a known weight of pure lime into sulphate, would make it 40.26. The number 40 may be safely adopted.

10. *Carbon*.—The determination of the combining proportion of carbon formed the subject of a series of laborious researches by Dumas and Stas. They burned graphite, diamond, and charcoal in a current of pure oxygen with scrupulous care. 1.375 grammes of diamond gave 5.041 of carbonic anhydride ( $CO_2$ ); and the mean of their results, which agreed very closely with each other, entitles us to fix the atomic weight of carbon at 12. Similar experiments by Erdmann and Marchand gave

them the number 12.014; and the results obtained by Liebig and Redtenbacher from the combustion of the oxalate ( $\text{Ag}_2\text{C}_2\text{O}_4$ ), the acetate, the racemate, and the tartrate of silver, correspond to 12.12, which coincides so nearly with the number deduced from those of Dumas, that these chemists themselves have adopted the number which he employs.

11. *Chlorine*.—Numerous careful experiments have been made with a view to determine the combining proportion of chlorine. De Marignac found that 100 parts of potassic chlorate ( $\text{KClO}_3$ ), when decomposed by heat, left 60.839 of potassic chloride ( $\text{KCl}$ ); and 22.032 of pure silver required 15.216 of potassic chloride for its complete precipitation. 14.427 of potassic chloride gave 27.749 of argentic chloride ( $\text{AgCl}$ ). Berzelius calculates from these results that the atomic weight of chlorine is 35.46; and this coincides exactly with the recent elaborate experiments of Stas; a result arrived at also by Penny 30 years ago.

Maumené, by heating argentic chloride in a current of hydrogen, found that 100 parts of silver were united with 32.856 of chlorine. The same chemist obtained from 100 parts of potassic chlorate 60.791 of potassic chloride; and from 100 parts of potassic chloride, he obtained by precipitation 192.75 of argentic chloride. These experiments furnish data from which the atomic weights of potassium and silver may be determined, as well as that of chlorine, in the manner following:—

The composition of potassic chlorate is represented by the formula  $\text{KClO}_3$ ; when heated it gives off the whole of its 3 atoms of oxygen. The atom of potassic chloride therefore will be the quantity which is combined with 48 parts (or 3 atoms) of oxygen. Now, taking Maumené's result that 39.209 parts of oxygen are combined in potassic chlorate with 60.791 of potassic chloride we have—

$$39.209 : 48 :: 60.791 : x (=74.4208, 1 \text{ at. of KCl}).$$

If 100 parts of potassic chloride produce 192.75 of argentic chloride, 1 atom, or 74.4208, of potassic chloride will furnish 1 atom of argentic chloride. For—

$$100 : 192.75 :: 74.4208 : x (=143.446, 1 \text{ at. of AgCl});$$

and 132.856 of argentic chloride contain 32.856 of chlorine; consequently (1 atom of argentic chloride containing 1 atom of chlorine), we find the atomic weight of chlorine as follows;—

$$132.856 : 32.856 :: 143.446 : x (=35.476):$$



but the atomic weight of argentic chloride being . . . = 143'446  
 that of silver is found by deducting the at. wt. of Cl . . . = 35'476

leaving the atomic weight of silver . . . . . = 107'970

and the atomic weight of potassic chloride being . . . = 74'4208  
 deduct from it the atomic weight of chlorine . . . = 35'476

we obtain the atomic weight of potassium . . . = 38'9448  
 No material error can therefore arise if the atomic weight of  
 chlorine be taken as . . . . . = 35'5  
 that of silver as . . . . . = 108'0  
 and that of potassium as . . . . . = 39'0

Dumas has also checked these numbers by burning finely divided silver in a current of perfectly dry chlorine. He thus found that 108 parts of silver combined with 35'505 of chlorine as a mean of two experiments.

12. *Chromium*.—The atomic weight of chromium was determined by Berlin, by converting argentic chromate ( $\text{Ag}_2\text{CrO}_4$ ) into argentic chloride; the number calculated from this result is 52'694; and that deduced from the reduction of the chromic anhydride ( $\text{CrO}_3$ ) to chromic sesquioxide, in the same series of experiments, is 52'54. Péligot's experiments on the acetate would make it between 52 and 53'6, but he considers 52'48 as nearest the truth; we have therefore adopted the number 52'5.

13. *Cobalt*.—Rothoff found that 269'2 parts of cobalt oxide ( $\text{CoO}$ ), when converted into chloride ( $\text{CoCl}_2$ ) by means of hydrochloric acid and precipitated by means of argentic nitrate, gave 1029'9 of argentic chloride: hence the atomic weight of cobalt is 58'98. The number 59'08 is the mean of five experiments made in a similar way by Dumas. Schneider, however, subsequently, from the decomposition of the oxalate, obtained results corresponding to the number 60; but the more recent experiments of Russell confirm the former number, and show that the atomic weight of cobalt is 58'74, or identical with that of nickel.

14. *Copper*.—Berzelius obtained from 7'68075 grammes of cupric oxide ( $\text{CuO}$ ), which were reduced in a current of hydrogen, 6'13075 of metallic copper; hence the atomic weight of the metal is 63'5. Erdmann and Marchand, by a similar method, obtained numbers which would make it 63'52.

15. *Fluorine*.—Berzelius found that 100 parts of fluor-spar ( $\text{CaF}_2$ ) when heated with an excess of sulphuric acid, yielded 175

of calcic sulphate ( $\text{CaSO}_4$ ). Louyet, on repeating this experiment, obtained 174·361 parts of calcic sulphate. The atomic weight of fluorine deduced from this latter result is 19. (See p. 163.) And these results have been confirmed by Dumas, who made similar experiments upon the fluorides of calcium, potassium, and sodium.

16. *Glucinum*.—Awdejew found that 100 parts of the chloride of this metal contained 88·42 of chlorine; hence, if the chloride be represented as  $\text{Gl}_2\text{Cl}_3$ , the combining number of the metal will be 6·97; but if the chloride be regarded as  $\text{GCl}_2$ , as assumed in this work, the atomic weight of the metal is 9·30.

17. *Gold*.—Berzelius, by reducing the potassio-auric chloride ( $\text{KCl}, \text{AuCl}_3$ ) in a current of hydrogen, determined the combining number of this metal at 196·66. By an earlier series of experiments he found that 142·9 of metallic mercury precipitated 93·55 of gold from the trichloride ( $\text{AuCl}_3$ ); 3 atoms of mercury causing the precipitation of 2 atoms of gold: and assuming the atomic weight of mercury to be 200, this would make the number for gold 196·44.

18.—*Hydrogen*.—The atomic weight of hydrogen was determined with great care by Dumas, by the method already described at p. 56. He ascertained, as a mean of nineteen experiments, that 8 parts of oxygen combined with 1·0012 of hydrogen to form water; the lowest quantity which these experiments gave being 0·9984, the highest 1·0045. The quantity of water collected in each of these experiments was considerable, varying from 230 to 1150 grains (15 to 75 grammes). Erdmann and Marchand repeated these experiments with similar results. Berzelius and Dulong concluded, from researches performed long previously upon a similar principle, though on a smaller scale, that the quantity of hydrogen united with 8 parts of oxygen was 0·9984, which coincides with the lowest number obtained by Dumas. It is obvious that no appreciable error can be committed by assuming hydrogen to possess an atomic weight of 1, that of oxygen being 16, if water be taken as  $\text{H}_2\text{O}$ .

19. *Iodine*.—De Marignac determined the number for iodine by a process analogous to that which he employed for chlorine. The atomic weight of potassic iodide ( $\text{KI}$ ) he fixed at 165·951; deducting from this 38·95, Maumené's number for potassium, we obtain 127 as the combining number of iodine. Dumas, from two experiments upon argentic iodide, which he converted into chloride by heating it in a current of dry chlorine, obtained the same result.

20. *Iridium*.—Berzelius deduced the number for iridium from an analysis of the potassio-iridic chloride ( $2\text{KCl}, \text{IrCl}_4$ ); his results would make it 197.12, which is identical with the number obtained for platinum.

21. *Iron*.—Berzelius found that 1.586 grammes of pure iron converted first into nitrate, and then into sesquioxide by ignition, gave 2.265 of sesquioxide ( $\text{Fe}_2\text{O}_3$ ); and Svanberg and Norlin, by reducing ferric oxide in a current of hydrogen, obtained from 35.783 of sesquioxide, 25.059 of metallic iron; making the atomic weight of iron 56.08. Erdmann and Marchand, by the method last named, fixed the atomic weight at 56.002, and Maumené has also arrived at a similar result by dissolving iron in aqua regia, and precipitating the sesquioxide by means of ammonia. Still more recently, Dumas has corroborated the same number by decomposing both the chlorides of iron by means of argentic nitrate—the mean of his four experiments giving 56.14.

22. *Lead*.—21.9425 grms. of plumbic oxide ( $\text{PbO}$ ) were reduced by Berzelius in a current of hydrogen, and gave 20.3695 of metallic lead: from the mean of his five experiments, the atomic weight of the metal would be 207.14. This result has been confirmed by De Marignac, who obtained, by the precipitation of 5 grammes of plumbic chloride ( $\text{PbCl}_2$ ) 3.8835 of argentic chloride, similar experiments by Dumas would make the number for lead 207.1, whilst from those of Stas it would be 206.912.

23. *Lithium*.—The number obtained by Berzelius for this metal, by neutralizing fused lithic carbonate ( $\text{Li}_2\text{CO}_3$ ) with sulphuric acid, is probably inaccurate, as this carbonate has subsequently been found to lose a little of its acid when melted. Mallett estimates the atomic weight of lithium at 6.97. Diehl, from an analysis of the carbonate, obtained the number 7.026; and Troost, from the chloride, obtained the number 7.01, as well as by decomposition of the carbonate by means of silica; 7.00 is therefore the number adopted.

24. *Magnesium*.—Berzelius found that 100 parts of magnesia, dissolved in pure sulphuric acid and ignited, gave 293.985 of magnesian sulphate ( $\text{MgSO}_4$ ); hence the atomic weight of magnesium would be 25.3; but this result is probably a little too high.

Scheerer, by ascertaining the quantity of baric sulphate produced by a given weight of magnesian sulphate, determined the number for magnesium at 24.22. The results of Svanberg and Nordenfeldt, by the decomposition of magnesian oxalate ( $\text{MgC}_2\text{O}_4, 2\text{H}_2\text{O}$ ) by heat, made it 24.7; those by converting a known weight of magnesia into sulphate, gave it as 24.74: whilst those of Mar-

chand and Scheerer, by ignition of the native carbonate, indicated the number 24.04. Dumas found extraordinary difficulty in procuring magnesian chloride quite free from magnesia. The mean of eleven experiments upon the precipitation of the chloride ( $\text{MgCl}_2$ ) by argentic nitrate gave 24.6 as the combining number of magnesium. The mean of these results is 24.32, but there is room for further experiment upon the exact number for this metal.

25. *Manganese*.—4.20775 of manganous chloride ( $\text{MnCl}_2$ ) gave Berzelius 9.575 of argentic chloride; the atomic weight of the metal, from a mean of two such experiments, is 55.14. Dumas, as a mean of five such experiments conducted in a similar manner, obtained the number 54.96.

26. *Mercury*.—Erdmann and Marchand obtained from 118.3938 grammes of mercuric oxide ( $\text{HgO}$ ) 109.6308 of mercury; a mean of five experiments gave 200.2 as the atomic weight of the metal. It may be safely estimated at 200.

27. *Molybdenum*.—Berzelius regarded the number originally given by himself for this metal only as an approximation. Svanberg and Struve, from an extensive series of experiments, considered that the most accurate results were obtained by roasting the molybdous disulphide in air, and they conclude that 100 parts of the disulphide ( $\text{MoS}_2$ ) yield 89.732 of molybdic anhydride ( $\text{MoO}_3$ ); hence, if the atomic weight of sulphur be taken at 32, that of molybdenum will be 92.12. Berlin, from the quantity of molybdic anhydride left by the salt  $(\text{H}_4\text{N})_4\text{O}_{2.5}\text{MoO}_3 \cdot 3\text{H}_2\text{O}$ , found the number for the metal (from a mean of four experiments) to be 91.96. Dumas, however, by reducing crystallized molybdic anhydride in a current of hydrogen, found, as a mean of five concordant experiments, 96 as the number for this metal.

28. *Nickel*.—Rothoff converted 188 parts of nickel oxide into chloride ( $\text{NiCl}_2$ ), and obtained from it 718.2 of argentic chloride; the number for nickel hence deduced is 59.08; and Dumas, as a mean of five experiments on the same plan, obtained the number 59.02. Russell found it by reducing the oxide in a current of hydrogen 58.738.

29. *Nitrogen*.—De Marignac, by converting 200 grammes of silver into nitrate ( $\text{AgNO}_3$ ), obtained 314.894 of the salt; 14.110 of argentic nitrate required for precipitation 6.191 of potassic chloride; 10.339 of silver converted into nitrate required 5.120 of ammoniac chloride for complete precipitation; the mean result, as calculated by Berzelius from several experiments performed in this manner, gives 14.004 as the number for nitrogen. Stas, by synthetic experiments upon argentic nitrate, fixed it at

14.044. Anderson, by the decomposition of argentic nitrate by heat, concluded that the atomic weight of nitrogen was 13.95; and Svanberg, from the analysis of plumbic nitrate ( $\text{Pb}_2\text{NO}_3$ ), obtained the same result: the number for nitrogen may therefore be taken as 14.

30. *Osmium*.—The atomic weight of this metal was calculated by Berzelius from the result obtained by heating the potassio-osmic chloride ( $2\text{KCl}, \text{OsCl}_4$ ) in a current of hydrogen, 1.3165 grammes of the salt leaving 0.401 gramme of KCl and 0.535 grm. of osmium: hence the number for osmium may be estimated at 198.8, which agrees with the later researches of Dumas.

31. *Oxygen*.—The atomic weight of oxygen is the fundamental one from which all others are calculated. Reasons have already been fully given which lead to the adoption of 16 as the atomic weight of oxygen, if that of hydrogen be taken as 1.

32. *Palladium*.—The number of this metal rests upon the authority of Berzelius, who found, by reducing the chloride of potassium and palladium ( $2\text{KCl}, \text{PdCl}_2$ ) in a current of hydrogen, that 2.606 grms. of the salt gave 0.563 gramme of chlorine, 0.851 of palladium, and 1.192 of potassic chloride: hence the atomic weight of palladium is 106.48.

33. *Phosphorus*.—According to Pelouze, a solution of 100 parts of silver in nitric acid is required to precipitate the chlorine from 42.74 of trichloride of phosphorus ( $\text{PCl}_3$ ); the atomic weight of phosphorus, therefore, would be 32.02. Berzelius, from the silver reduced from argentic sulphate by a known weight of phosphorus, estimated the number for phosphorus at 31.36; and Schrötter concludes—from a mean of ten experiments, in which phosphorus was burned in a current of dry air, and thus converted into phosphoric anhydride—that the true atomic weight is 31; a result confirmed by careful experiments upon the trichloride by Dumas, who found it to be 31.03.

34. *Platinum*.—Berzelius found that 6.981 grammes of the potassio-platinic chloride ( $2\text{KCl}, \text{PtCl}_4$ ), when reduced in a current of hydrogen, gave 4.957 of a mixture of platinum and potassic chloride; 2.822 of this was platinum: hence the number for platinum is 197.12, identical with that of iridium.

35. *Potassium*.—De Marignac's experiments on the potassic chlorate ( $\text{KClO}_3$ , related when speaking of the atomic weight of chlorine) gave the number for potassium, 39.1; those of Maumené, 38.95; those of Pelouze, 39.14; and those of Stas, 39.137. It may therefore be taken as 39.1.

36. *Rhodium*.—3.146 grms. of the potassio-rhodic chloride

(KCl,RoCl<sub>3</sub>) when heated in a current of hydrogen, were found by Berzelius to furnish 0.912 grm. of rhodium, and 0.515 grm. of potassic chloride; whence the atomic weight of the metal should be 104.32.

37. *Selenium*.—100 parts of selenium, when heated in a current of chlorine, yield exactly 279 of selenious chloride (SeCl<sub>2</sub>), according to Berzelius, which would make the atomic weight 79.32; but the method employed is not perfectly trustworthy. Dumas, by modifying the method of proceeding, obtained as a mean of seven experiments, 79.46.

38. *Silicon*.—Berzelius found that 100 parts of silicon, when oxidized, yielded 208 parts of silica, which, if taken as SiO<sub>2</sub>, would give an atomic weight of 29.62; this appears to be too high. Pelouze states that a solution of 3.685 parts of silver in nitric acid precipitated 1.454 of silicic chloride (SiCl<sub>4</sub>), whence the number would be 28.48; and Dumas, by a mean of two experiments conducted on the same principle, obtained the number 28.02: further experiments are however desirable upon an element of such importance.

39. *Silver*.—The combining number of this metal has been repeatedly determined with very great care, as it forms a fundamental datum in these inquiries. De Marignac, by precipitation of a known weight of silver from its solution in nitric acid, as chloride (AgCl) estimates the equivalent as 107.97; and the experiments of Pelouze and of Maumené agree almost exactly with this result. Dumas has also confirmed this result by burning finely divided silver in a current of chlorine gas; and the number deduced by Stas, from his experiments, was 107.930. 108 may therefore be taken as the atomic weight of silver.

40. *Sodium*.—Berzelius found that 100 parts of sodic chloride (NaCl) gave by precipitation 244.6 of argentic chloride, the atomic weight of sodium would therefore be 23.17. Pelouze found, as a mean of three experiments, that 100 parts of silver required for precipitation 54.144 of sodic chloride, whence the atomic weight of sodium would be 22.97. Dumas, as a mean of seven experiments of a similar kind, obtained the number 23.01; and Stas found it to be 23.043. It may be taken as 23.

41. *Strontium*.—The number for this metal was also obtained by a similar method, viz., by ascertaining the proportion of silver which a given weight of strontic chloride (SrCl<sub>2</sub>) requires for precipitation. Stromeyer's experiments give the number 87.34; De Marignac's, 87.54; Pelouze's, 87.68; and the mean of a numerous series of experiments by Dumas, gives 87.48.

42. *Sulphur*.—The atomic weight of sulphur was estimated by Berzelius from the weight of plumbic sulphate formed by oxidizing a known weight of lead with nitric acid, and heating it with an excess of sulphuric acid till the weight ceased to alter. As a mean of three experiments, 100 parts of lead yielded 146.45 of plumbic sulphate ( $\text{PbSO}_4$ ); hence the atomic weight of sulphur would be 32.128; this result was confirmed by converting argentic chloride into sulphide in a current of dry sulphuretted hydrogen. Erdmann and Marchand, by distilling cinnabar with copper turnings, obtained from 100 parts of cinnabar, 86.213 of mercury as a mean of two experiments. This would make the atomic weight of sulphur exactly 32—a result which agrees with those of Dumas, who converted a given weight of silver into sulphide, by heating the metal in the vapour of sulphur. As a mean of five such experiments, he obtained the number 32.02, while Stas found it to be 32.0742.

43. *Tellurium*.—1.5715 gramme of tellurium when oxidized by nitric acid and heated till the excess of nitric acid was expelled, left a residue of  $\text{TeO}_2$ , which Berzelius found to weigh 1.9365 grm.; hence the number for tellurium would be 128.30. But Dumas, from experiments not hitherto published in detail, gives figures which would make it 129.

44. *Tin*.—100 parts of tin, when oxidized by nitric acid and ignited, were found by Berzelius to yield 127.2 parts of stannic oxide ( $\text{SnO}_2$ ); from which the number for tin would be 117.64. Mulder states that he obtained from 100 parts of this metal 127.56 of stannic oxide, which would give the number 116.1. Dumas, on repeating this experiment, obtained the number 118.06 for the metal, and this result was confirmed by experiments on the quantity of silver required for the precipitation of a known weight of stannic chloride ( $\text{SnCl}_4$ ). The atomic weight of tin may therefore be taken at 118.

45. *Titanium*.—The number for this metal rests upon the analysis of its tetrachloride. Rose found, as a mean of four experiments, that 100 parts of the tetrachloride ( $\text{TiCl}_4$ ) contained 74.46 of chlorine, which would give 48.24 as the atomic weight of titanium. Later experiments by Isidore Pierre, in which 0.8215 gramme of  $\text{TiCl}_4$  furnished 1.84523 gramme of  $\text{AgCl}$ , seem to fix it at 50.34.

46. *Tungsten*.—The number 189.28, calculated from the experiments of Berzelius, was only an approximation. Schneider, on repeating the experiment of reducing tungstic anhydride ( $\text{WO}_3$ ), in a current of hydrogen, found that 100 parts of the an-

hydride yielded 79·316 of the metal, and on oxidizing metallic tungsten, and reconverting it into tungstic anhydride, he found 79·327 parts of metal furnished 100 of anhydride: the atomic weight of tungsten from the mean of these results would be 184·12. Marchand, by similar experiments, fixed it at 184·1, a result completely confirmed by Dumas. It may be taken as 184. Persoz, however, has endeavoured to show, though without much probability, that tungstic anhydride consists of  $TuO_5$ , not of  $WO_3$ , and in such case the atomic weight of tungsten,  $Tu$ , would be 153·3. (See *note*, p. 649.)

47. *Uranium*.—Some doubt exists as to the exact combining number of this metal. Wertheim's experiments on the double acetate of sodium and uranium would give 118·48; and Ebelmen's on the oxalate 118·86; but Péligot's estimate, which would make it 120, is usually adopted.

48. *Vanadium*.—The atomic weight of this metal was determined by heating vanadic anhydride ( $V_2O_5$ ) in a current of hydrogen. It was thus reduced to the sesquioxide. Berzelius found as a mean of four experiments, that 120·927 parts of the anhydride lost thus 20·927 of oxygen. Roscoe found that also as a mean of four experiments 121·22 parts of the anhydride lost by reduction to sesquioxide in a current of hydrogen 21·22 of oxygen, and he calculated the atomic weight of the metal from this at 51·362; while from seventeen experiments on the oxychloride ( $VOCl_3$ ) he obtained 61·276 of chlorine in 100 parts: from these experiments the atomic weight would be 51·05, and as a mean of the two series he adopts 51·3. (See p. 653.)

49. *Zinc*.—Favre's experiments on the analysis of zincic oxalate, and on the quantity of hydrogen which a given weight of zinc liberates during its solution in hydrochloric acid, would make the atomic weight of the metal 66·0; and Jacquelin, by the decomposition of the nitrate and of the sulphate of zinc ( $ZnSO_4$ ) by heat, obtained results corresponding to the number 66·24. The original experiments of Berzelius on this metal lead to the number 64·5. Subsequently, A. Erdmann prepared a pure zincic oxide, mixed it with pure charcoal obtained from sugar, and distilled the zinc in a current of hydrogen; he then oxidized the metal by nitric acid, and converted it into oxide by ignition. The atomic weight of zinc, calculated from a mean of four experiments conducted in this manner, is 65·04. The same number is obtained from the analysis of zincic lactate by Pelouze.

50. *Zirconium*.—As a mean of six experiments, Berzelius found that 100 parts of sulphuric anhydride ( $SO_3$ ) required 75·853 of



zirconia, in order to form the sulphate of the earth. Zirconic fluoride forms with potassic fluoride two compounds: in one the fluorine is combined with zirconium and potassium in equal quantity; in the other the quantity of fluorine combined with zirconium is 3, if that with potassium is 2: hence Berzelius considered that zirconia contains  $\text{Zr}_2\text{O}_3$ , and the combining number of the metal is 67·18, but De Marignac has shown that zirconia is more probably  $\text{ZrO}_2$ , in which case the number would be 89·5.

(1015) *Table of Combining Numbers.*—We may here sum up the foregoing results, by stating that the following numbers may be taken, for the purpose of calculation, as representing the atomic weights of the elementary bodies on the hydrogen scale. They differ but very slightly from the numbers given at pages 24 and 25 of Part I.:—

Aluminum ...	27·5	Hydrogen ...	1·0	Rhodium ...	104·3
Antimony ...	122·0	Indium ...	72 (?)	Rubidium ...	85·3
Arsenicum ...	75·0	Iodine ...	127·0	Ruthenium ...	104·2
Barium ...	137·0	Iridium ...	197·1	Selenium ...	79·5
Bismuth ...	210·0	Iron ...	56·0	Silicon ...	28·0
Boron ...	10·9	Lanthanum ...	92·0	Silver ...	108·0
Bromine ...	80·0	Lead ...	207·0	Sodium ...	23·0
Cadmium ...	112·0	Lithium ...	7·0	Strontium ...	87·5
Cæsium ...	133·0	Magnesium ...	24·3	Sulphur ...	32·0
Calcium ...	40·0	Manganese ...	55·0	Tantalum ...	182·0
Carbon ...	12·0	Mercury ...	200·0	Tellurium ...	129·0
Cerium ...	92·0	Molybdenum ...	96·0	Thallium ...	204·0
Chlorine ...	35·5	Nickel ...	59·0	Thorium ...	238·0
Chromium ...	52·5	Niobium ...	94·0	Tin ...	118·0
Cobalt ...	59·0	Nitrogen ...	14·0	Titanium ...	50·0
Copper ...	63·5	Osmium ...	199·0	Tungsten ...	184·0
Didymium ...	96·0	Oxygen ...	16·0	Uranium ...	120·0
Erbium ...	114·6	Palladium ...	106·5	Vanadium ...	51·3
Fluorine ...	19·0	Phosphorus ...	31·0	Yttrium ...	61·7
Glucinum ...	9·5	Platinum ...	197·1	Zinc ...	65·0
Gold ...	196·6	Potassium ...	39·1	Zirconium ...	89·5

(1016) *On the Numerical Relations of the Proportional Numbers of the Elements.*—Several years ago Prout started the idea that the numbers which represent the combining proportions of the different elementary bodies are multiples by whole numbers of the combining proportion of hydrogen; and he attributed the various cases of apparent departure from this proposition to inaccuracy in the experimental determinations of the combining proportion of the exceptional bodies. Since that period an increased degree of precision has been attained in experiments of this nature, and many of the apparent exceptions to Prout's idea have been removed.

Independently of the importance of accurate determinations of

these numbers for the purposes of chemical analysis, and for the tracing out of quantitative relations between the chemical equivalents and certain physical properties, such as the density and specific heat of the simple and compound bodies, the verification or disproof of Prout's hypothesis acquires a high interest from its connexion with the nature of the elementary bodies themselves; for if the combining proportions of all the elements be multiples by whole numbers of the combining proportion of hydrogen, it is not absolutely impossible that the various bodies at present regarded as elementary, may in reality be *compounds* of a single primordial substance condensed in different degrees in the various so-called elements.

If experiment justifies the hypothesis of Prout, it would be possible that the three following propositions were true:—

*a.* Similar quantities of this one elementary principle might, by variety in the mode of their arrangement, form bodies (at present regarded as elementary) or radicles of equal atomic weight, but endowed with distinct properties.

*b.* A radicle, intermediate in properties and in its combining number between two other radicles of the same group, might be produced by the union of half a molecule of the two extreme radicles.

*c.* And, finally, the supposed constitution of these radicles (or bodies at present regarded as simple) might be assimilated to the compound radicles of organic chemistry of known constitution. There would be, however, this important distinction between the radicles of mineral chemistry and those of organic origin; viz., that the radicles of inorganic chemistry possess a stability indefinitely greater than those of the organic creation—a stability, indeed, of such an order, that the present resources of analytical chemistry are insufficient to effect their decomposition.

The probability, on the other hand, of such views would obviously be negatived if the elements exhibited no such multiple relation in their equivalents.

(1017) Certain remarkable relations which exist between many of these numbers have been pointed out by various chemists. The whole subject of atomic weights was a few years ago submitted to a careful revision by Dumas (*Ann. de Chimie*, III. lv. 129). As the result of his investigations and calculations, Dumas concludes that, in a modified sense, Prout's law is true; and he considers that the elementary bodies, the atomic weights of which he regards as accurately known, may be arranged in three groups, or

rather two groups, if the duplication of the atomic weights adopted in this work be followed—viz.,

1. Bodies which are represented by multiples of a whole number of the atomic weight of hydrogen.

2. Multiples by the number 0.5 of that of hydrogen.

1. Bodies which are multiples by a whole number of the atomic weight of hydrogen:—

Hydrogen ... ..	1	Arsenicum ... ..	75
Carbon ... ..	12	Bromine ... ..	80
Nitrogen ... ..	14	Molybdenum ... ..	96
Oxygen ... ..	16	Silver ... ..	108
Fluorine ... ..	19	Cadmium ... ..	112
Sodium ... ..	23	Tin ... ..	118
Silicon ... ..	28	Antimony ... ..	122
Phosphorus ... ..	31	Iodine ... ..	127
Sulphur ... ..	32	Tellurium ... ..	129
Calcium ... ..	40	Barium ... ..	137
Manganese ... ..	55	Tungsten ... ..	184
Iron ... ..	56	Osmium ... ..	199
Cobalt ... ..	59	Mercury ... ..	200
Nickel ... ..	59	Lead ... ..	207
Zinc ... ..	65	Bismuth ... ..	210

2. Multiples by 0.5 of the atomic weight of hydrogen.

Aluminum ... ..	27.5	Selenium ... ..	79.5
Chlorine ... ..	35.5	Strontium ... ..	87.5
Copper ... ..	63.5		

The relations exhibited between the numbers of many of these bodies which are chemically allied are often very remarkable:—

1. It has been observed that, in several instances where two elements are in close chemical relation to each other, they have atomic weights which are identical; this happens, for example, with the following pairs of bodies:—

Cobalt and nickel ... ..	59
Lanthanum and cerium ... ..	92
Rhodium and ruthenium ... ..	104.2
Platinum and iridium ... ..	197.1

2. In other cases, the ratio of the atomic weights is as 1 to 2; for instance:—

Oxygen = 16	Sulphur = 32
Aluminum = 27.5	Manganese = 55

3. It has also been stated that, where three elements belong to the same natural group, the atomic weight of the intermediate

element is frequently equal to the mean of those of the two extremes. This is true in the case of

$$\begin{array}{lcl} \text{Lithium} & = & 7\cdot02 \\ \text{Sodium} & = & 23\cdot04 \\ \text{Potassium} & = & 39\cdot13 \end{array} \quad ; \quad \frac{7\cdot02 + 39\cdot13}{2} = 23\cdot07;$$

the number for sodium being the arithmetic mean of those for lithium and potassium: but this is the only case in which this relation is rigidly in accordance with the experimental numbers. Several groups agree very nearly with such a supposition, but the divergence is, notwithstanding, too great to admit of being attributed to errors of experiment. For example:—

$$\begin{array}{lcl} \text{Calcium} & = & 40 \\ \text{Strontium} & = & 87\cdot5 \\ \text{Barium} & = & 137\cdot0 \end{array} \quad ; \quad \frac{40 + 87\cdot5}{2} = 88\cdot5$$

$$\begin{array}{lcl} \text{Sulphur} & = & 32 \\ \text{Selenium} & = & 79\cdot5 \\ \text{Tellurium} & = & 129\cdot0 \end{array} \quad ; \quad \frac{32 + 129}{2} = 80\cdot5$$

In both these groups, the difference between the experimental and the calculated number of the intermediate elements amounts to 1·0; and it is probable that this difference is physically true.

In cases like the lithium and calcium groups, it has been suggested, both by Pettenkofer and by Dumas, that the relation between the different members of the group may be analogous to that observed in bodies of organic origin which belong to the same homologous series. The reader who is desirous of pursuing this speculation will find it ably and clearly discussed by Dumas in his paper already cited (*Ann. de Chimie*, III. lv. 164).

(1018) *Experiments of Stas on Atomic Weights.*—Stas, however, arrives at a conclusion respecting Prout's hypothesis entirely opposite to that of Dumas. He has lately published two memoirs (*Trans. Brussels Acad. Sci.* 1860, 1865) containing the results of a long and most laborious series of researches, which it appears almost impossible to surpass in precision. In the last memoir (p. 23), he gives the following numbers for some of the most important elements (O=16):—

Oxygen	...	...	16·000	Chlorine	...	...	35·457
Silver	...	...	107·930	Bromine	...	...	79·952
Lead	...	...	206·912	Iodine	...	...	126·850
Potassium	...	...	39·137	Nitrogen	...	...	14·044
Sodium	...	...	23·043	Sulphur	...	...	32·074
Lithium	...	...	7·022				

The numbers for lead and sulphur are founded upon experiments in the earlier memoir.

These results have been obtained in each case by several dif-

ferent processes ; and the differences between the various numbers thus arrived at for the same body are in all cases much smaller than the difference between the mean result and the whole number required by Prout's law. These numbers were obtained by operating with balances of unusual delicacy, and upon quantities much larger than is customary in researches of this kind—the quantities amounting in some cases to nearly a pound weight of the materials.

The numbers thus obtained do not differ from those of Dumas, or indeed from those in general use, sufficiently to affect any calculations of analyses founded upon them ; but from the variety of methods employed, and the extraordinary degree of care and precision with which the experiments were made, the results are of the highest value in relation to the hypothesis of Prout.

Stas concludes his first memoir with these words :—

“ So long as we adhere to the results of experiment for the establishment of the laws by which matter is governed, we ought to consider the law of Prout as a pure illusion, and should regard the indecomposable substances of our globe as distinct bodies, having no simple relations between their atomic weights. The undeniable analogy in properties which is observed in certain of the elements must be sought for in other cases than those derivable from the relations in weight of their acting masses.”

In his second memoir he further says, at p. 23 : “ To resume and to conclude, I have inquired whether the law of chemical proportion is a *limited* law, or a law of rigorous accuracy. I think that I have proved that it is the expression of a mathematical relation. I think also that I have shown that the atomic weight of the same body determined by the aid of different elements, and by methods independent of each other—a weight which *ought* to be identical in each case, *is* so in reality within the limits of accuracy which it is possible by our present methods of investigation to attain.”

We cannot too jealously watch any twisting of experimental data to suit our theories ; and those who are familiar with the speculations on the numerical relations of the atomic weights, cannot but feel that the severe method of induction from facts has in this case been more than usually departed from by the followers of a science which is pre-eminently one of experiment.

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END OF PART II.













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